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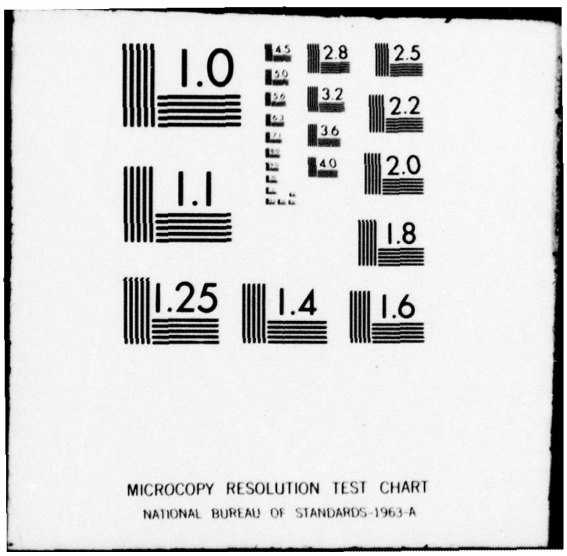
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HOLOGRAPHIC OPTICAL ELEMENT MATERIALS RESEARCH

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An experimental program was conducted to study and improve the achievable holographic index modulation in dichromated gelatin suitable for producing high-quality holographic optical elements. Emphasis was placed on gaining a working knowledge of the chemical and physical processes involved in dichromated gelatin image production. The largest improvement in index modulation was achieved with the application of dicarboxylic acid salts. Index modulation could be increased by up to 150% per

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) unit of light exposure over conventional processing methods by taking advantage of unipointly attached reduced chromium complexes. We confirmed the usefulness of the sol temperature as a measure of bulk cross-linking in gelatin. With polycarboxylic acids, index modulations of 0.16 were obtained in reflection holograms. These resulted from cracks formed between holographic fringe planes. The cross-link sites, which are the carboxyl groups on the gelatin molecues, need not be present initially for image formation and are probably formed during the photoreduction of dicromate. Increases in cross-linking were not achieved by supplying a larger population of carboxyl groups in the film layers. Depending on the processing conditions, reflection holograms can exhibit broad-band or narrow-band wavelength reflectance. We found that control of film swelling during development is essential for controlling the holographic image and scattering-noise formation. Swelling of the layers is influenced by the pH, temperature, and solute content of the wash water. We studied the formation of optical scattering noise caused by alcohol precipitation in both gelatin sols and film layers. The precipitation or optical denaturation is influenced by solution salt and detergent content, pH, and the molecular weight of the gelatin present. Highest diffraction efficiency and lowest scattering noise are achieved with pH adjustment to the acid side. A study of various dehydrating agents used in holographic development showed that the lower alkanols are best for index modulation formation and suppression of scattering noise. A thoery for the mechanism of image formation is presented that postulates the sequential formation of a chemical, small void, and large crack holographic grating. This theory is designed to reconcile the seemingly conficting experimental results obtained by various investigations. Some novel experiments that shed light on the mechanism of image formation are also presented and are explained in terms of this theory.

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PREFACE

This report covers the work accomplished during the period January 1976 through July 1978 under Contract F44620-76-C-0064, entitled "Holographic Optical Element Materials Research." The work was supported by the United States Air Force Office of Scientific Research (AFOSR), Bolling Air Force Base, Washington, D.C. The technical monitor was Capt. John Neff of AFOSR.

The work was accomplished by the Exploratory Studies Department of Hughes Research Laboratories, a division of Hughes Aircraft Company, under the direction of Dr. Donald H. Close. The program manager was Mr. Andrejs Graube, with the technical assistance of Mr. Cesar C. DeAnda, Mr. Angel F. Banuelos, Mr. Thomas S. Taylor, and Mr. Mark A. Mulvihill.

SECTION 1

INTRODUCTION AND SUMMARY

The objective of this program was to conduct research on the chemical and physical aspects of dichromated gelatin (DCG) film preparation and use, with the primary objective of improving holographic index modulation per unit of light exposure. The photosensitive material was required to have high optical quality and low scattering noise. Emphasis was placed on these characteristics since they are necessary for the application of DCG to hologram optics fabrication.

The practical application of holographic lenses to many optical systems demands a thick phase hologram recording material with a large index modulation and good sensitivity. Surveys of existing holographic materials [1-3] show that there are only two materials that exhibit index modulations larger than 0.02: bleached silver halide emulsions and DCG. When the additional requirements of (1) permanence, (2) resolution, (3) environmental endurance, (4) optical quality, and (5) lack of scattering noise are considered, only DCG meets the demanded characteristics.

To provide additional background and orientation for this program, we briefly review here the structure, properties, and applications of holographic optical elements, such as those fabricated from DCG.

Holographic optical elements operate by diffraction rather than by refraction or reflection.[4] They are produced by exposure of a suitable light-sensitive recording material to a fine scale optical interference pattern. The pattern is formed by splitting a laser beam into two parts, expanding and shaping these two beams, and directing them simultaneously onto the recording material. If the pattern is stable during the exposure time and the recording material has adequate spatial resolution, a high contrast recording of the pattern is achieved. This pattern is locally periodic, so the element can be characterized as a grating structure. Light diffracting from the grating is the desired image light in the optical system. This light can be made to focus, with varying imaging properties, depending on the grating characteristics, which in turn depend on the geometry of the two original recording beams.

The following seven points summarize the unique characteristics of holographic optical elements:

- Holographic elements are relatively lightweight and low cost, especially for large apertures, because they exist as thin films and are made by a simple light exposure.
- Since multiple holograms can be recorded in a single layer of recording material, spatially overlapping elements are possible.
- The optical function of the holographic element is to a first approximation independent of substrate geometry. This shape independence allows unusual geometries.
- The imaging characteristics of holographic elements vary rapidly with wavelength. For example, the focal power increases in direct proportion to the operating wavelength.
- Since element function is by diffracted light, optical efficiency is not inherent and becomes a primary system consideration.
- If an optical system has a holographic element, it is inherently three optical systems: the "main" system and two auxiliary optical systems (one for each hologram construction beam).
- A single holographic element, like a single conventional element, cannot perform functions of a system of several components. For example, a single element has only unit angular magnification.

These characteristics and their interactions provide both advantages and disadvantages for any particular application. In general, holographic elements will replace some conventional elements, especially when larger apertures are required. However, the major uses of holographic elements will be special, unique applications. Usually, a holographic element will be found in an optical system with conventional elements operating over a relatively narrow spectral bandwidth.

Some of the unique optical functions that holographic elements provide are: dual-purpose (common-aperture) optics, unusual geometrical configurations, and narrow spectral or angular response. If a unique functional application can be combined with the features of lightness and low cost, then major advantages can be realized. Application areas where some or all of the advantages can be realized include near IR detection systems, visual displays, multiple imaging systems, dichroic beam splitters and mirrors, and multiple wavelength systems.

One example of the application of holographic optical elements is the head-up display (HUD).[5-7] In this application, the important features of holographic elements are lightness, shape independence, dual function, high efficiency with narrow spectral bandwidth, and low scattering and residual absorption. The holographic element is used to provide simultaneously the combining function and the final collimating function for the HUD.

Many applications of hologram optics require hologram recording materials that have several common characteristics. Of these properties, index modulation and light sensitivity are most important.

The index modulation Δn for each hologram is calculated from the equations[8]

$$\sqrt{\eta_o} = \tanh\left(\frac{\pi \Delta n d}{\lambda_c \sin \theta'/2}\right) \qquad (1)$$

$$\sqrt{\eta_o} = \sin\left(\frac{\pi \Delta n d}{\lambda_c \cos \theta'/2}\right) \qquad (2)$$

for reflection and transmission elements, respectively, where η_o is the peak diffraction efficiency, d is the film thickness, λ_c is the reconstruction wavelength, and θ' is the interior included angle between the beams. The major motivation for this program was to develop chemical methods to provide a large index modulation in DCG. Since the terms λ_c and θ' are usually defined by the optical design, the product of Δn and d must be used to maximize diffraction efficiency.

The complexity of the DCG process dictated an experimental approach toward achieving these objectives. This approach was based on 5 years of previous experience with DCG. In particular, this prior work, along with the results of investigations by others, produced a theory of the

DCG process that has guided the research on this program. This theory includes postulated mechanisms for cross-linking gelatin molecules to provide index modulation; for denaturating gelatin in alcohol solutions to introduce scattering noise; and of film dynamics during swelling and contraction, which must be controlled to provide uniformity and stability.

The body of this report examines in detail the various film preparation and processing techniques that were performed to meet these objectives. Many processing methods were investigated during this program, and the most promising techniques were investigated in depth, optimized, and reduced to holographic practice.

Section 2 describes the highly successful application of the bifunctional organic compounds (the dicarboxylic acid salts) to improving index modulation. Specific results show the methods by which these compounds can be applied to cross-linking improvement.

Section 3 provides results and discussion of fundamental experiments on gelatin carboxyl group manipulation and image formation. These experiments were performed to both enhance DCG cross-linking and to provide a better understanding of the processes involved in image formation. We used the sol temperature as a primary measure of molecular cross-linking and confirmed its applicability in gelatin film hardening experiments; this is discussed in Section 4.

The dynamics of gelatin film swelling and its control as a function of pH, temperature, and solutes are covered in Section 5. The optical denaturation of gelatin in alcohol solutions under a wide variety of experimental conditions is presented in Section 6. Section 7 summarizes the results obtained from using various dehydrating agents in the DCG development process. A theory of image formation in DCG holograms is presented in Section 8 along with experiments that provide evidence for its support.

The research accomplished on this program significantly improved the understanding of the DCG process and provided a substantial body of new experimental data on DCG. This improved understanding has greatly benefited holographic display development programs by aiding in developing techniques for film processing and stabilization. With the improved understanding, we have successfully demonstrated a DCG process that can produce large-aperture display elements that possess excellent uniformity and environmental stability.

SECTION 2

DICARBOXYLIC ACID SALTS

The formation of a reduced chromium cross-link in DCG requires the presence of two carboxyl groups on separate gelatin molecules. The bridging material, a low-valence chromium complex, in DCG cross-links is formed in a photochemical reaction, as shown in Figure 1. Although the exact composition of the low-valence chromium material is not known, its presence in hardened gelatin has been amply demonstrated.

Due to steric hindrances in cross-link formation, at least 90% of the chromium bound in even completely hardened collagen or gelatin is still (unipointly) attached to only one carboxyl group. Only about 10% of the chromium complexes form intermolecular crosslinks.[9] The chromium complexes functioning as the cross-linking agents are to be found among the small amount of bipointly fixed chromium. Figure 2 shows the waste of most of the reduced chromium sites that occurs in completely hardened gelatin. In the figure, only two of the reduced chromiums act as intermolecular cross-links; the rest of the chromiums are unipointly attached. Clearly, if more of the unipointly attached chromiums could be utilized as cross-links, then a stronger holographic image could be formed in DCG without requiring additional light exposure.

In the leather tanning industry, we encounter a situation very similar to the one that we have with DCG. Animal hides, which are mainly composed of collagen, are treated with low-valence chromium compounds. The low-valence chromium cross-links the collagen molecules into the stable structure that we all know as leather. It is claimed that the size of the chromium complex is a chief factor in tanning. The requirements for tanning are that the complex must be of a satisfactory molecular size and there must be coordination between the hydroxyl groups attached to the chromium and the active groups in the collagen.[10] Since one or both of these requirements may not be met in any particular chemical situation, leather tanners have used certain additives to their low-valence chromium treatment baths to obtain better chrome fixation within the tanned leather. Among these additives are dicarboxylic acid

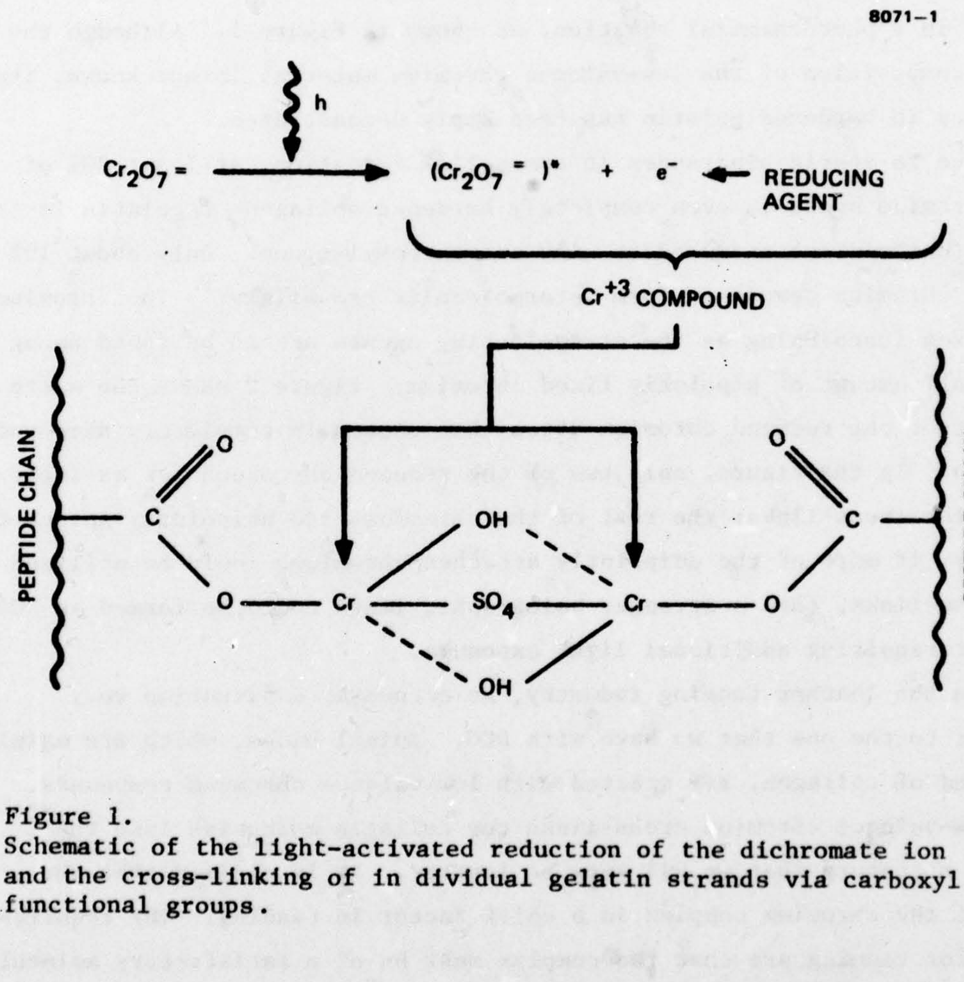

Figure 1.
Schematic of the light-activated reduction of the dichromate ion and the cross-linking of in dividual gelatin strands via carboxyl functional groups.

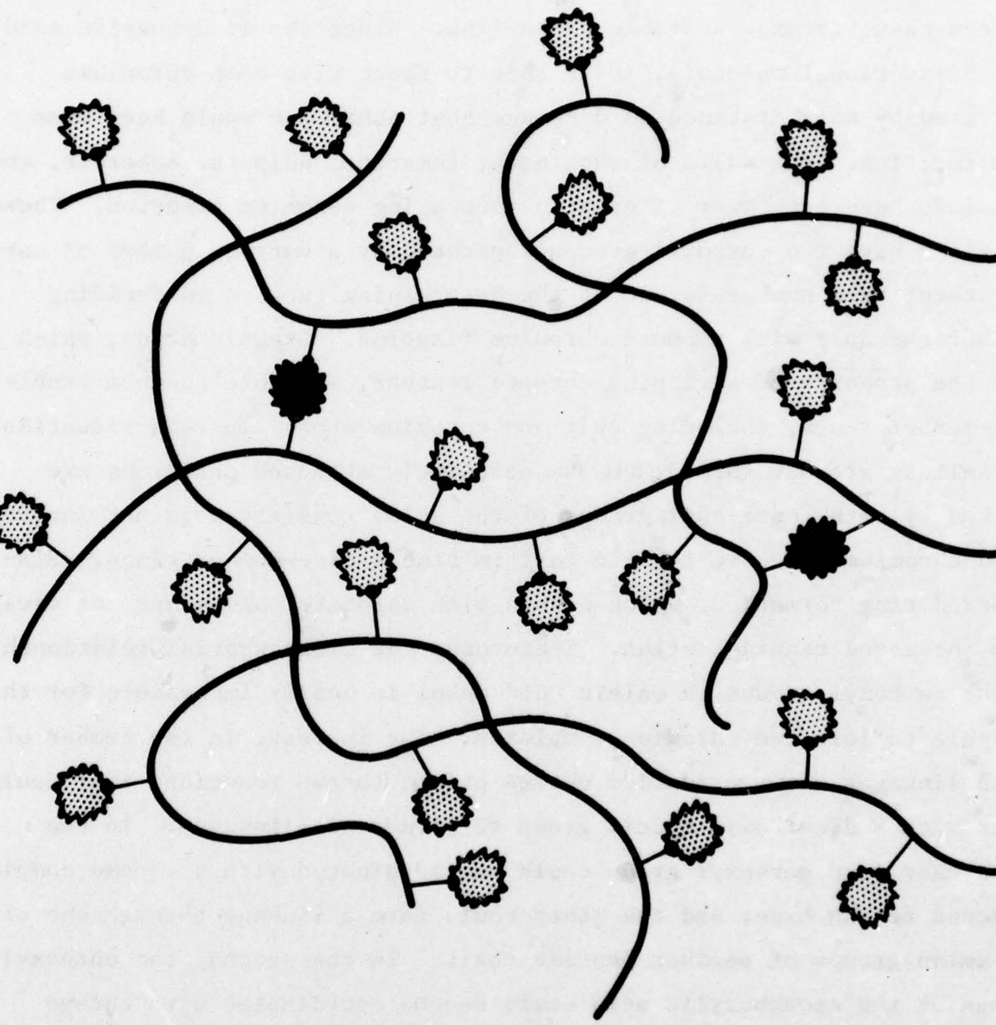

Figure 2. Schematic of the small relative population of reduced chromium intermolecular cross-links (solid areas) among the many unipointly attached species (dotted compounds).

salts (DCASs).[11] The idea behind using DCASs as crosslink enhancers is illustrated in Figure 3. The figure shows two unipointly attached chromiums on separate gelatin strands and a DCAS bridging the gap between them, forming a stable cross-link. Since the dicarboxylic acid is a bifunctional molecule, it is able to react with both chromiums separated by some distance, a distance that otherwise would keep them from reacting. The salts of succinate, fumarate, adipate, suberate, and phthalate have the power of greatly increasing chromium fixation. These materials have two carboxyl groups separated by a varying number of carbon atoms; this number is one of the determining factors in deciding whether the salt will promote chromium fixation. Organic acids, which have the property of stripping chromed leather, are able to form stable five-member rings, including only one chromium atom. In this situation, cross-links are not formed, but the unipointly attached chromiums are blocked by both functional groups of the acid. Oxalate does not increase fixed chromium since it is able to form stable five-member rings. Six-membered ring formation, which occurs with malonate, also does not usually show increased tanning action. Therefore, the close spatial relationship of the carboxyl groups in maleic acid makes it nearly impossible for this molecule to join two chromium complexes. The increase in the number of cross-linkages between peptide chains points to two reactions that could occur with a dicarboxylic acid group to form cross-linkages. In the first case, one carboxyl group could be coordinated with a chrome complex attached to the hide, and the other could form a linkage through one of the amino groups of another peptide chain. In the second, the carboxyl groups of the dicarboxylic acid could become coordinated with chrome complexes attached to different peptide chains and thus build up additional cross-linkages. Considerable amounts of dicarboxylic amino acids; aspartic and glutamic acids; and, of the basic amino acids, lycine, arginine, and histidine have been found in gelatin. These are now known to be responsible for many of the properties of gelatin, as they form side chains to the main peptide chains. We believe that, in a similar fashion, the DCASs form bridges between unipointly fixed chromium, which would otherwise be sterically prevented from forming cross-links.

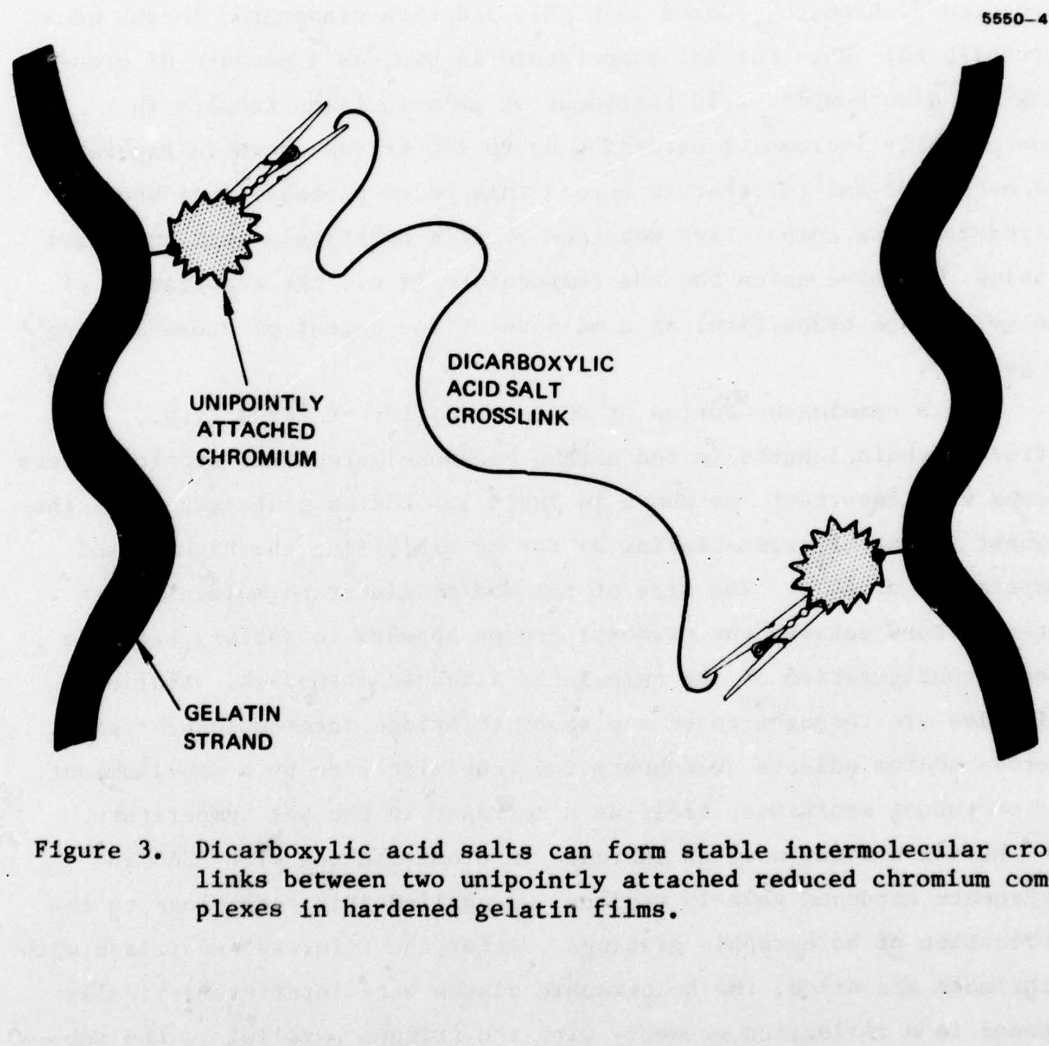

Figure 3. **Dicarboxylic acid salts can form stable intermolecular crosslinks between two unipointly attached reduced chromium complexes in hardened gelatin films.**

In our work, we have found that DCASs can lead to increased cross-linking in exposed DCG films.[12] In applying this method, the DCG layers are exposed to laser light in the usual manner, washed in water to remove unreacted dichromate, soaked in DCASs, and then dehydrated in the usual alcohol bath. When the sol temperature is used as a measure of cross-linking, dicarboxylic acid treatment of gelatin films results in monotonically increasing hardening up to 100 hr, as shown in Figure 4. The decreased sol temperature beyond this point probably indicates an increase in the competitive reaction of film hydrolysis with prolonged soaking. We have taken the sol temperature (i.e., the temperature of the gel-to-sol transition) as a measure of the extent of cross-linking in gelatin.

When a homologous series of DCASs of different sizes (i.e., different chain lengths in the carbon backbone) are used, steric effects become very important, as shown in Table 1. Sodium glutarate shows the highest amount of cross-linking by far by exhibiting the highest sol temperature of 60°C. The size of the sodium glutarate molecule with three carbons between the carboxyl groups appears to satisfy best the steric configuration of the unipointly attached chromiums. Smaller molecules are throught to be too short to bridge inter-molecular gaps, whereas sodium adipate overshoots the requisite size by a small amount. The overshoot manifests itself as a decrease in the sol temperature.

Having demonstrated an increase in cross-linking with DCAS in dichromate hardened gelatin regions, we applied this technology to the fabrication of holographic gratings. After the film was sensitized with dichromate and dried, the holographic plates were interferometrically exposed in a reflection geometry with the fringes parallel to the substrate and washed with deionized water. Sodium sulfate was added to the DCAS soaking solutions to limit film swelling and to prevent distortion of the holographic gratings during the chemical treatment.

To determine the optimum solution composition for the film swelling retardant, sodium sulfate, we applied the DCAS sodium succinate in a wide range of retardant concentrations, as shown in Figure 5. Index modulation is maximized in a broad region between approximately 1.5 and

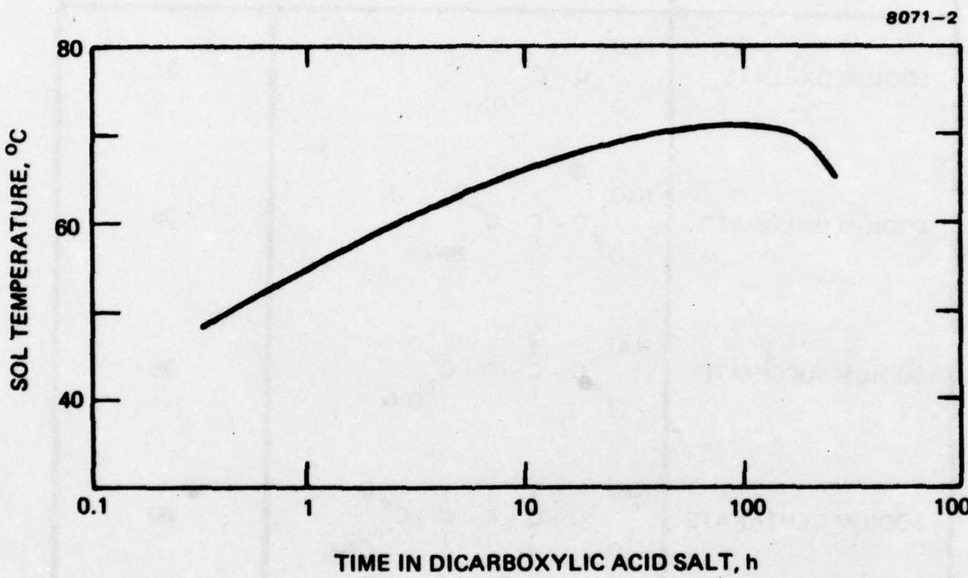

Figure 4. Increase in gelatin film cross-linking measured as sol temperature as a function of reaction time in dicarboxylic acid salt solution.

Table 1. Dicarboxylic Acid Salts and Their Influence on Gelatin Film Sol Temperature

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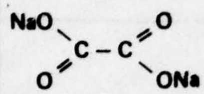
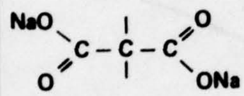
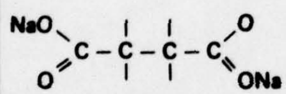
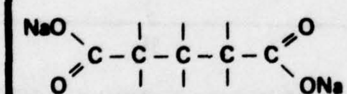
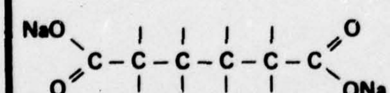
ACID SALT	STRUCTURE	SOL TEMPERATURE, °C
SODIUM OXALATE		37
SODIUM MALONATE		39
SODIUM SUCCINATE		35
SODIUM GLUTARATE		60
SODIUM ADIPATE		46

Figure 5. Index modulation achieved in DCG reflection holograms as a function of sodium sulfate concentration.

2.5 molar. In later experiments, we consistently used 2.0 molar sodium sulfate to prevent excessive film swelling.

Having selected very concentrated solutions of sodium sulfate as the swelling retardant, we chose sodium succinate as the DCAS for investigation. Figure 6 shows that index modulation in the holographic grating can be more than doubled by the application of sodium succinate. This figure also shows that relatively large concentrations of sodium succinate are best for producing increased index modulation. After approximately 50 mM,increases in sodium succinate concentration do not significantly augment index modulation. It could be argued that the increases in index modulation are caused by film hydrolysis of the unhardened regions, which would increase the differential of hardening between the exposed and unexposed fringes. This would also be manifest as increased index modulation in the developed hologram. To investigate this possibility, we subjected two sets of holograms to two different treatments. In one, DCAS was applied; in the other, only a sodium sulfate solution of the same concentration as in the first solution was applied. Figure 7 conclusively shows that the DCAS-treated holograms exhibited much more index modulation than did those in the control group. Actually, index modulation decreased in the control group after approximately 100 min of soaking. This decrease points to the onset of hydrolysis of the gelatin film, causing disruption of the grating structure. Figure 7 shows that the DCAS treatment of the holographic film increased the index modulation by more than 150% from that of the untreated control group. Although it does not definitely prove that DCASs are the chemical species acting on unipointly fixed chromiums, it does point to the differential chemical effect that DCAS has on the film, and it does show that large chemical differences do exist in DCG between the exposed and unexposed regions of the film after holographic exposure.

These results point to the value of using DCAS for cross-link enhancement. Significantly more index modulation can be gained from the

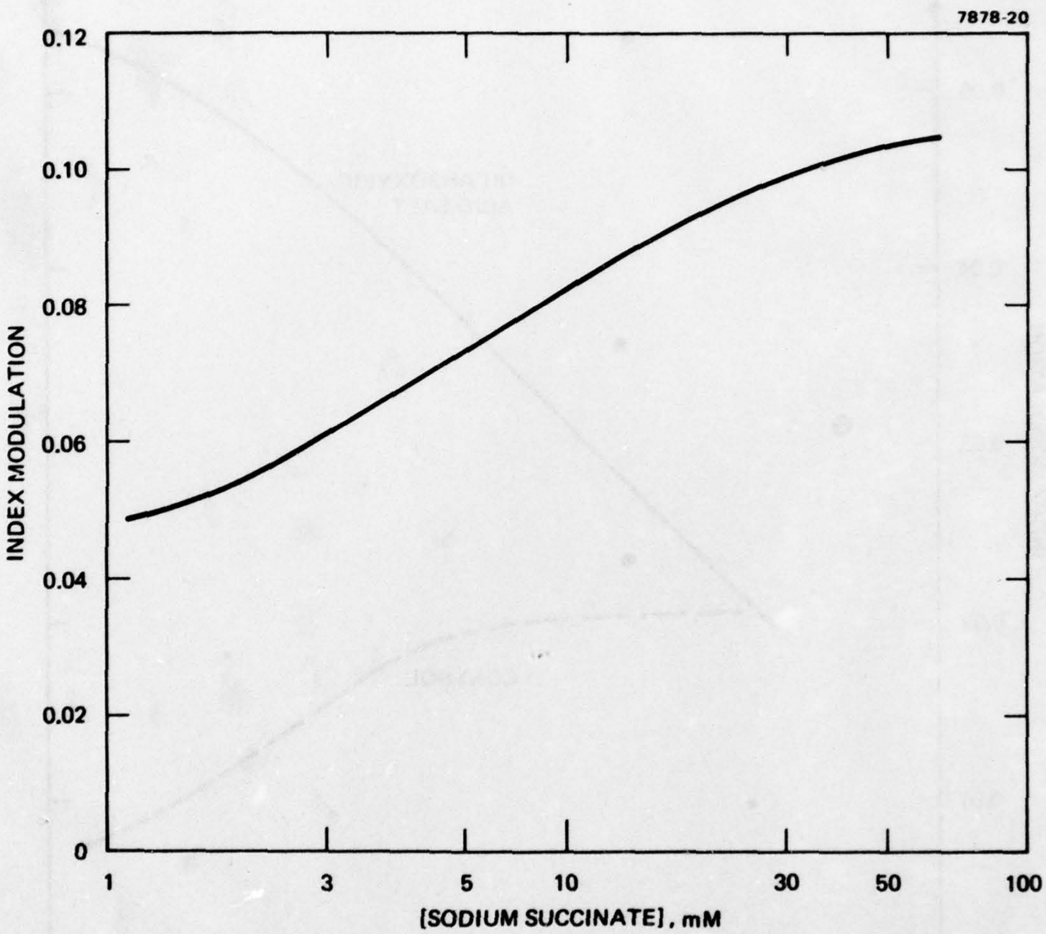


Figure 6. Reflection hologram index modulation as a function of sodium succinate concentration in the processing solution.

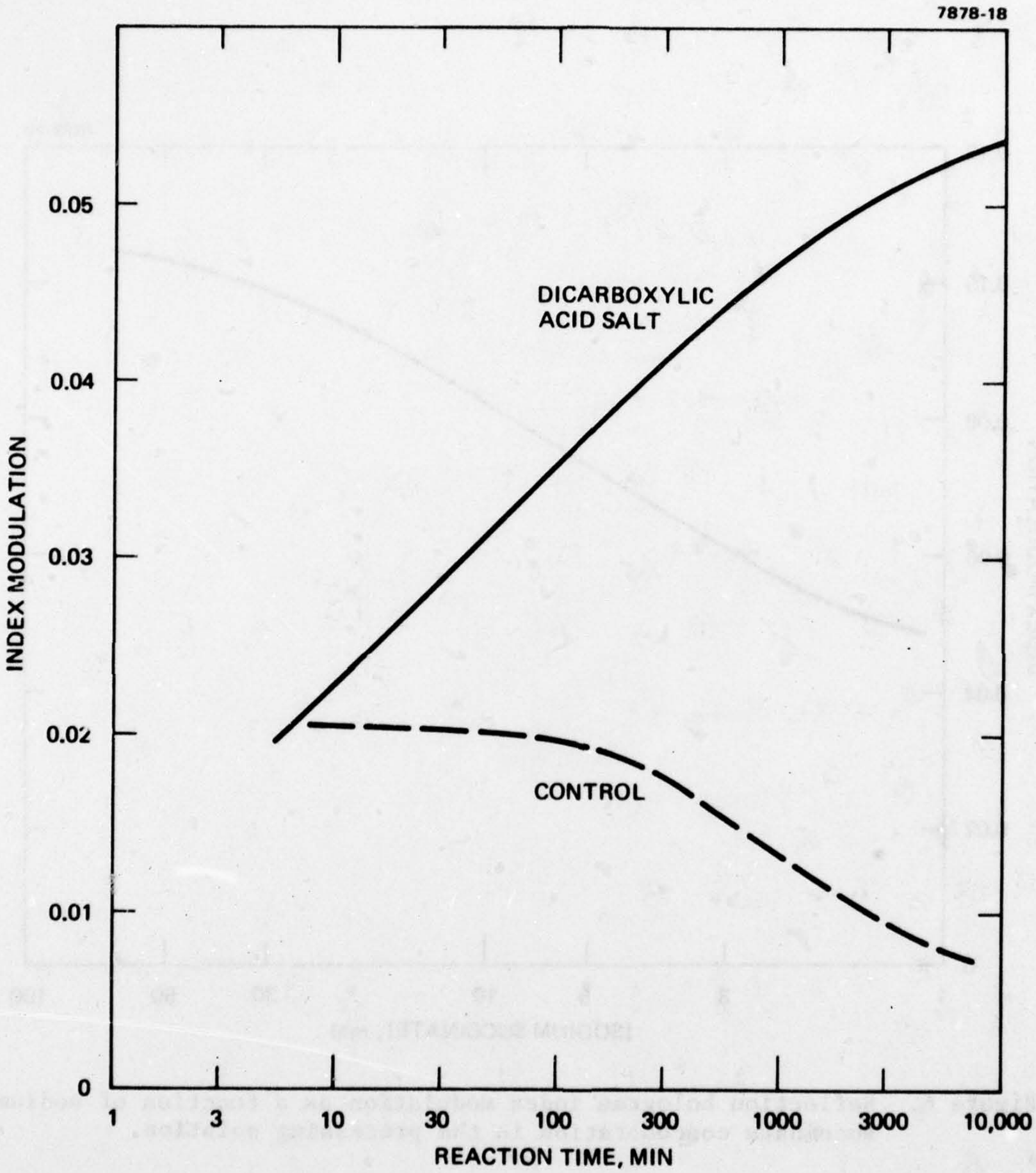


Figure 7. Index modulation produced in reflective holographic gratings as a function of reaction time with and without DCAS.

DCAS-treated holograms per unit exposure in the holographic film. The central role of film swelling control is also evident. Optimum DCAS cross-linking can occur only if the gelatin molecular separations are on the order of the size of the DCAS molecule used. As a practical recipe, we propose the method outlined in Table 2.

The pH adjustment in Step 2 is used to ensure that the ionic environment within the gelatin will be reproducible from hardening solution to hardening solution. The wash in Step 3 is used to remove unreacted ammonium dichromate from the layer. A seven-day soaking time in the hardening solution is recommended in Step 4 because Figures 4 and 7 show that there is little to be gained by a longer soak. In Step 5, the deionized water wash is used to remove the swelling-restraining salt, sodium sulfate, and the unreacted sodium succinate. In Steps 6 and 7, which are conventional DCG processing steps, temperature may be adjusted to obtain the desired diffraction efficiency (see Section 5.B). Although the procedure outlined in Table 2 worked very successfully for our holograms, its universal application to all DCG holograms should be taken with some caution. The amount of swelling that takes place in Step 4 of Table 2 will depend on the overall hardness or cross-linking of the DCG layer. In relatively soft layers, the swelling will still be large despite the high concentration of sodium sulfate present. Osmotic forces will force the gelatin molecules far apart, and sodium succinate molecules may not be able to bridge the gap between the reduced chromium sites on individual gelatin strands. In this case, the DCAS may more effectively form intra-molecular links rather than inter-molecular cross-links. Intra-molecular links would contribute very little to the differential hardening between exposed and unexposed fringes. The soaking in the hardening solution with soft gelatin films may show decreased index modulation in this case, as shown in Figure 7, where the control group holograms show decreased index modulation due to the hydrolysis of the gelatin layer. Perhaps the best way to define which DCAS molecules to use is to start with sodium succinate and look for increased index modulation. If increased modulation is not seen, then larger molecules should be attempted (sodium adipate, etc.).

TABLE 2

Procedure for Applying DCAS to DCG Holograms

Step 1.	Prepare a solution containing 2.0 M sodium sulfate and 50 mM sodium succinate.
Step 2.	Adjust the pH of the solution to 4.5 with concentrated sodium hydroxide.
Step 3.	Wash exposed DCG holograms in deionized water for 3 min.
Step 4.	Soak holograms in prepared hardening solution for 7 days at room temperature.
Step 5.	Wash hologram in deionized water for 5 min at room temperature.
Step 6.	Dehydrate in 2-propanol for 5 min at room temperature.
Step 7.	Dry in low relative humidity atmosphere (<10%RH).

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We also explored the improved utilization of chromium sites by the use of polycarboxylic acid salts and DCAS mixtures. The idea with DCAS mixtures was to use a variety of DCAS sizes in the same solution so that the DCAS of the proper size would bridge the intermolecular gelatin strand distance regardless of the extent of swelling. We also used polycarboxylic acid salts, which are molecules that have several carboxyl functional groups. We reasoned that the probability of cross-link formation would greatly increase as the number of carboxyl functional groups of each molecule increased. Many steric combinations between any two carboxyl functional groups are possible, although intra-molecular bonds may also result. Additionally, polycarboxylic acid salts are capable, at least in theory, of cross-linking more than one pair of unipointly attached chromium complexes. In order of increasing effectiveness, we found that the monosodium salt of glutamic acid; nitrilotriacetic acid; citric acid; a mixture of glutaric, adipic, and succinic acids; potassium biphthalate; terephthalic acid; and aspartic acid were effective in increasing cross-linking in DCG holograms. The mixture of glutaric, adipic, and succinic acid salts did not produce as much increased cross-linking as did succinic acid by itself. This was probably due to intra-molecular links formed by the shorter dicarboxylic acids. The dicarboxylic acids and tricarboxylic acids containing a nitrogen atom with an unshared pair of electrons (such as nitrilotriacetic acid and the sodium salt of glutamic acid) do not show as good a cross-linking response as do the straight dicarboxylic acids. Although the nitrogen atoms on these molecules may facilitate the diffusion of these species into the gelatin layer, their cross-linking capacity evidently is not increased by them. The best index modulation achieved was 0.162 with aspartic acid for a DCG layer of 10 μm thickness and having an optical density of 0.02 at a wavelength of 5145 Å during exposure and exposed for 120 mJ/cm^2. This index modulation represents a substantial increase over the index modulation achieved without dicarboxylic or polycarboxylic acid salt application.

The uncertainty in the index modulation measurement is about 10%, and it is dependent on the accuracy of the measurements of the terms in Eq. 1. We used a Cary 14R spectrophotometer to measure both η_o and λ_c, showing measurement uncertainties of about 5% and 0.5%, respectively. The geometrical factor θ' was very accurately held constant at 180°, providing a spatial frequency of about 5900 cycles/mm. Film thickness was accurately measured with a Sloan Dektak (a surface profile measurement instrument), indicating thickness variations of about 5%. These measurement uncertainties combined to give the variability to index modulation assessment.

SECTION 3

CARBOXYL GROUPS

The creation of a cross-link in DCG films requires the presence of three reacting species: one photo-reduced chromium complex and two carboxyl groups on spearate gelatin molecules. Since the amount of index modulation produced in DCG films is directly dependent on the differential of the number of cross-links present in exposed and unexposed areas, it is evident that the carboxyl groups play a major role in the maximization of the cross-links in exposed areas. As described below, we studied the effects of modifying the cross-link mechanism of the carboxyl groups on the gelatin molecules.

A. METHYLATED GELATIN

In the *leather tanning industry*, the dominant function of the ionized carboxyl groups of collagen for the fixation of trivalent chromium complexes has been shown experimentally.[9] Collagen with its carboxyl groups completely discharged loses its affinity for various low-valence chromium compounds completely. By total esterification of the carboxyl groups, the binding of low-valence chromium compounds is prevented.

Chrome tannage of animal hides generally has many chemical parallels in the DCG reaction. In both cases, the fibrous protein collagen is the starting material, and chromium compounds are used to cross-link individual linear polypeptide molecules. In leather manufacturing, however, the chromium is introduced into the hides in a low-valance, or reduced, state, whereas, in the DCG reaction, the chromium is reduced from valence 6 to 3 during the photo-activated reaction.

The binding of low-valence chromium compounds in leather tannage can be prevented by permanently masking the carboxyl groups through esterification. If esterification of the carboxyl groups on gelatin blocks the image-formation capability of dichromate compounds, the vital role of the initial presence of carboxyl groups in the photosensitive DCG films can be demonstrated.

We prepared esterified gelatin derivatives and tested their ability to record holographic images in DCG. Esterification was accomplished by methylation with methanol.[13] Ground gelatin was treated with concentrated sulfuric acid (0.036 N solution of sulfuric acid in absolute methanol) for more than 196 hr with intermittent agitation. The gelatin was then washed twice with absolute methanol, dried, and swollen in 10 times its own volume of water. Since powdered gelatin swollen in the water made the pH of the supernatant liquid below 2, it was titrated with 5 N sodium hydroxide, with stirring, until pH 6 was reached. The swollen granules were melted at 40°C to a clear liquid and set to a gel at 4°C. The gel was then ribboned, and the salts were removed from it by bathing in large quantities of deionized water. The ribbons were then dried, remelted at 50°C, and coated onto glass microscope slides. The DCG films fabricated from the esterified gelatin were holographically exposed and developed by the conventional water/alcohol method.

The resulting films contained efficiently diffracting holograms that qualitatively appeared the same as nonmethylated DCG holograms. However, the modified gelatin holograms contained much higher scattering noise levels, and the surface of the films appeared rough, as if partially dissolved away in the first development bath.

The important observation is that esterified gelatin is still capable of recording efficient images in the absence of ionized carboxyl groups. It appears that as the dichromate is reduced in the photoactivated reaction, the gelatin is oxidized to the point where carboxyl groups are created on the gelatin molecule. This in situ manufacture of carboxyls probably conveniently provides very localized cross-link attachment points for the reduced chromium compounds. An initial increase in the carboxyl population of a DCG film before exposure, therefore, would have no effect on film sensitivity or cross-link improvement.

The increased optical scattering noise observed in the methylated gelatin holograms was probably due to a general molecular deterioration of the film and a decrease in gelatin molecular weight during the methylation process. The sulfuric acid probably effectively hydrolyzed the polypeptide chains to reduce the molecular weight to less than one-third of the original molecular weight.[13] A reduction in molecular size makes the gelatin more prone to dissolution in the water development bath, and also more likely to form light-scattering centers by precipitation in the alcohol development bath (see Section 6).

B. CARBOXYL GROUP INCREASE

In Section 3.A, we saw that the esterification or blocking of the carboxyl groups in DCG films does not result in the loss of image formation capability. This implies that the carboxyl groups do not need to be present initially to record images. However, it can be reasoned that, if the population of the carboxyl groups is increased initially, the probability of cross-link formation for a reduced chromium complex may be increased by providing attachment points at more frequent intervals along the gelatin chains.

We investigated the effect of increases in carboxyl groups on the formation of cross-links in the DCG chemical system. Carboxyl groups were created in the gelatin by oxidizing the films with potassium permanganate.[14] We expected the side chains on the gelatin containing partially oxidized terminal carbon atoms, such as aldehyde or alcohol functional groups, to be fully oxidized to carboxyl groups.

The oxidation was carried out on both exposed and unexposed gelatin films, so that four different DCG conditions were tested: (1) unexposed, unoxidized; (2) exposed, unoxidized; (3) unexposed, oxidized; (4) exposed, oxidized. For each of these film types, the sol temperature was measured at the various experimental conditions.

The oxidizing solution contained 0.2 g of potassium permanganate, 15 g sodium carbonate, and 10 g sodium sulfate per 100 ml of solution. The sodium carbonate provided an alkali environment for the reaction, and the sodium sulfate was included to restrain the gelatin films from swelling excessively. The oxidizing treatment was applied at room temperature, followed by a deionized water wash and the measurement of the sol temperature.

Differences in sol temperature were recorded for the light exposed and unexposed films without oxidation, showing increased cross-linking for more exposed films. However, the differential sol temperature for the exposed and unexposed films with permanganate oxidation was very small and extremely hard to measure. The difficulty of the sol temperature measurement came from the extreme hardening of the gelatin film by the permanganate. In many of the films, the oxidation hardening forced the sol temperature over 100°C, and it was not practicable to measure the sol temperature.[14]

Variations of the oxidation treatment, consisting of diluting the permanganate concentration and lowering the pH from 11.3 to 5.7 with sulfuric acid, reduced the sol temperature of the resulting films to measurable levels. The difference in hardening effect between light-exposed and unexposed regions of oxidized films was not observed.

From these results, we conclude that the increase in carboxyl groups resulting from direct oxidation of gelatin films with permanganate does not increase the cross-linking in exposed DCG areas. The permanganate oxidation itself appears as a polymerization or cross-linking of the gelatin molecules, possibly without the intervention of bridging material.[14] These strong oxidation cross-linking effects prevent complete assessment of the role of increased carboxyl populations in the DCG system, but their initial presence in DCG films does not appear to be vital.

C. FILM CRYSTALLIZATION

In aqueous solution, gelatin molecules exist as single chains completely surrounded by water molecules. When a thin layer of a solution of gelatin is dried, a clear film is obtained with different microstructure and properties depending on the temperature of drying.[15] X-ray diffraction shows that films dried in hot air show a broad diffraction pattern typical of liquids or glassy materials.[16] On the other hand, films dried in cool air give an X-ray pattern with a series of diffracted arcs, indicating the presence of a definite crystalline species. The crystallinity in gelatin films is thought to result from the primary and secondary molecular structure.

Besides the amino acid building blocks, gelatin also contains polysaccharides and aldehydic derivatives, but these substances account for less than 1% of the total composition.[17] The absence of cystine or cysteine residues indicates that there is negligible disulfide covalent cross-linking between the linear molecules. The precise sequence of amino acids in gelatin chains has not been determined, but the general three-dimensional arrangement is clear. The three amino acids, glycine, proline, and hydroxyproline, account for about 55% of the gelatin molecule and occur in sequences that permit the formation of "crystalline units." These units, which are made by the wrapping of three gelatin molecules around each other in a rope-like fashion to form what is known as a triple-stranded helix,[15] are responsible for the crystallinity seen by X-ray diffraction. The helical conformation is held together by lateral hydrogen bonding between the three chains. Each individual hydrogen bond is not very strong, but since there are many of them, their sum total can produce rigid films. Figure 8 compares the crystallinities in two gelatin films that differ in only their thermal and drying histories.[15]

Up to about 20% crystallinity can exist in dry gelatin films, but several factors are known to reduce and even completely suppress the crystalline helix formation. Among these factors are the previous

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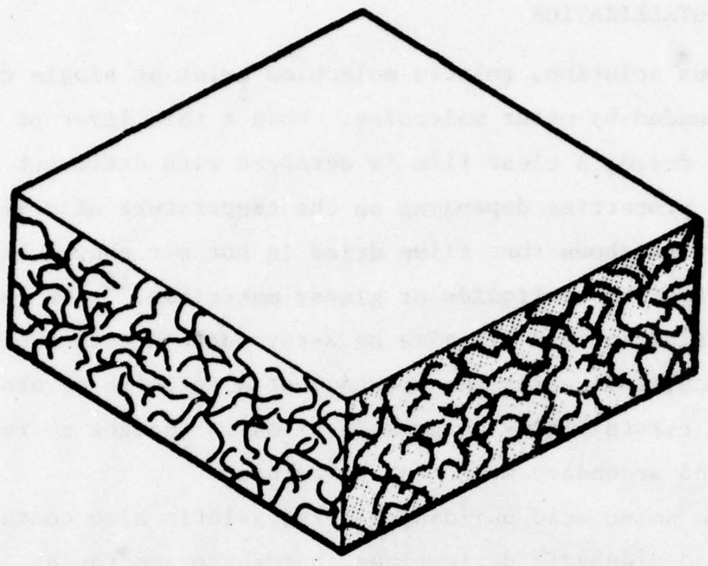
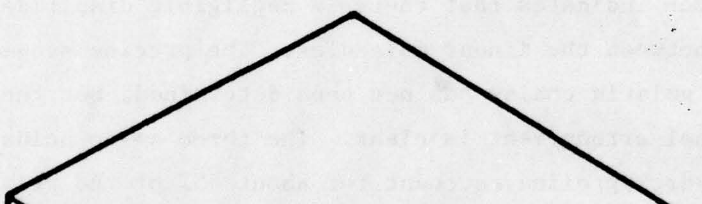


(a) AMORPHOUS FILM DRIED IN HOT AIR



(b) CRYSTALLINE FILM DRIED IN COOL AIR

Figure 8. Comparison of two gelatin films of (a) amorphous structure with minimal crystallinity, and (b) more ordered structure with maximum crystallinity.

thermal history of a film and the presence of salts and other compounds (see Section 5.C). The crystallinity is known to affect several gross gelatin film properties, including tensile strength and optical rotation of polarized light.[17]

In the noncrystalline gelatin regions, where the gelatin chains are single stranded, strong links can be formed between and within individual molecules with a variety of organic and inorganic compounds. Our laboratory results show that the cross-linking can proceed spontaneously with most cross-linking agents, although light or heat activation is required for dichromate. Cross-linking markedly decreases gelatin solubility, and, as in the case of crystallinity, it affects the mechanical and optical properties.

Holographic use of DCG films has shown that, with hot and cold drying, scattering noise centers are easily formed in the resulting gratings. Drying films at room temperature is recommended to reduce the tendency of amorphous film production, where random crack formation and gelatin precipitation are most likely to occur.[18]

The idea of film crystallinity was utilized further in our experiments for index modulation improvement. We reasoned that, since the crystallization of gelatin molecules segregates the polar and nonpolar regions of the gelatin strand, the reactive cross-link sites (the carboxyl groups) could be concentrated by crystallization.[15, 19] The inactive or hydrocarbon parts of the gelatin molecules would form the triple-stranded helix configuration, leaving the polar cross-link sites in segregated random orientations.

The process of crystal formation becomes manifest as the physically observable phenomenon of gelation. More perfect crystals and stronger gels are formed as a gel is allowed to stand at some temperature below the melting point.

We investigated the ability of aged gels with various amounts of crystallinity to produce index modulation in the DCG system. The temperature of the gelling layers was used as a second crossed variable.

Gelatin layers were allowed to gel from the sol for from 4 to 1850 min. After gelatin aging, DCG films were dried in the dark at 30% relative humidity for 2 hr, then exposed holographically and developed with the conventional water/alcohol method.[18]

Figure 9 shows a typical result of the effect of gelling time on light diffraction efficiency in the developed holograms. The diffraction efficiency is approximately constant for the various gelling times. It is thought that the formation of crystallites in the gelatin is extremely rapid, and the tendency for molecular association of the gelatin molecules is great. The short gelling time of 4 min is sufficient to form a gel in a thin layer with reasonable gel strength. Actually, the gelling time is about 30 min longer than indicated in Figure 9, since the film does not abruptly stop gelling when it begins to dry, but continues to gel as it dries.

The relatively constant diffraction efficiency that is achieved with gelling time shows that most of the carboxyl group segregation takes place after a few minutes of gelling. Hence, prolonged film crystallization cannot be recommended as a means for improving index modulation substantially. The slight decrease in diffraction efficiency with gelling time is probably due to the dark reaction of the dichromate. Although the dark reaction is much slower in gels than in dry films, it can not be stopped entirely.

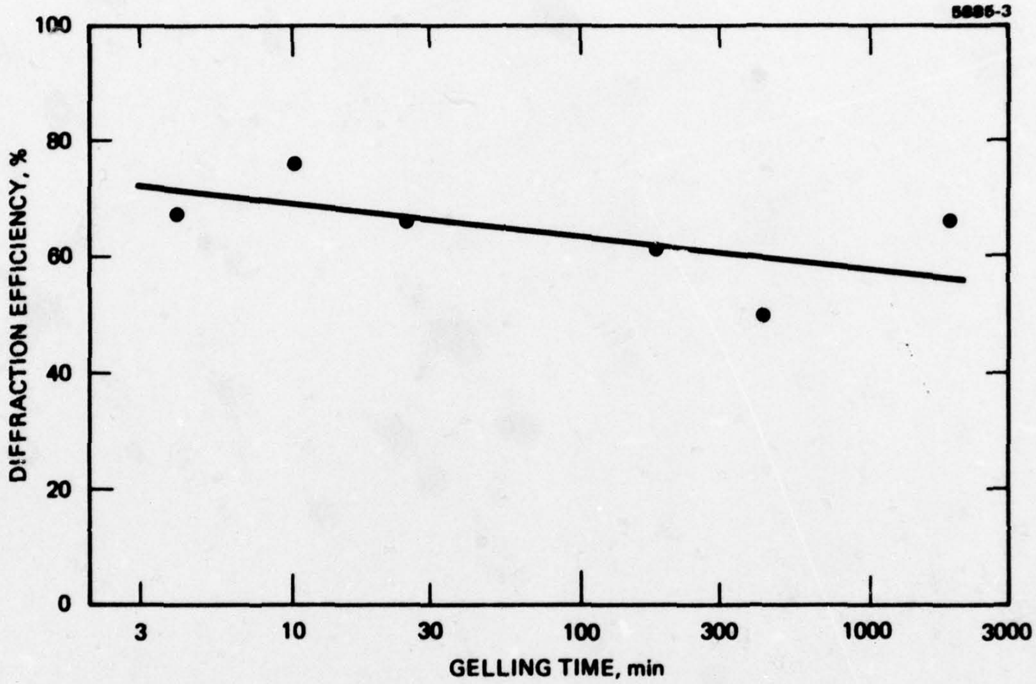


Figure 9. Light diffraction efficiency in DCG holograms as a function of film gelling time after coating.

SECTION 4

SOL TEMPERATURE

Previous investigators have used the sol temperature as a measure of intermolecular cross-linking in fibrous proteins.[20] Although the relationship between the number of cross-links in a particular film system and its sol temperature may deviate somewhat from linearity, it is certainly thought to be at least a monotonically increasing function. The sol temperature also provides a simple and reliable method for determining gelatin layer hardness.

We chose the parameter of sol temperature as a relative estimate of cross-linking in the DCG experiments and conducted several preliminary experiments to demonstrate its applicability to the DCG system.

Figure 10 shows that the sol temperature of freshly prepared DCG films increases with storage time. Because of the dark reaction, gelatin and dichromate combine without the benefit of actinic radiation.[21,22] The sol temperature increases as the dark-reaction cross-linking takes place. These film samples were stored at an elevated temperature to speed up the dark reaction, since its effect is not seen as rapidly at room temperature.

The number of cross-links formed in a DCG layer is also a function of the dichromate concentration in the film resulting from increased photoactivated cross-linking.[23] Figure 11 shows that increased dichromate concentration does produce increased cross-linking as measured by the increased sol temperature. From this data, we can conclude that sol temperature is a valid measure of DCG film cross-linking and is a sufficiently sensitive measure to reflect variations in film hardness.

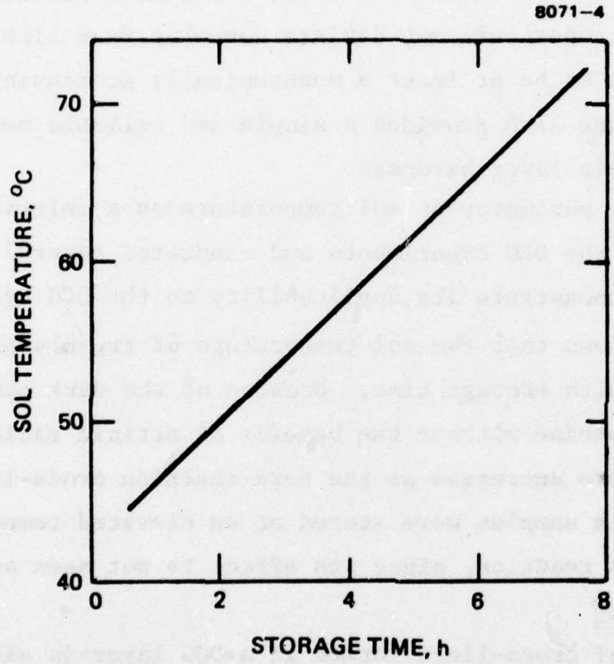


Figure 10.
Sol temperature of DCG films increases linearly with prolonged storage time in the dark.

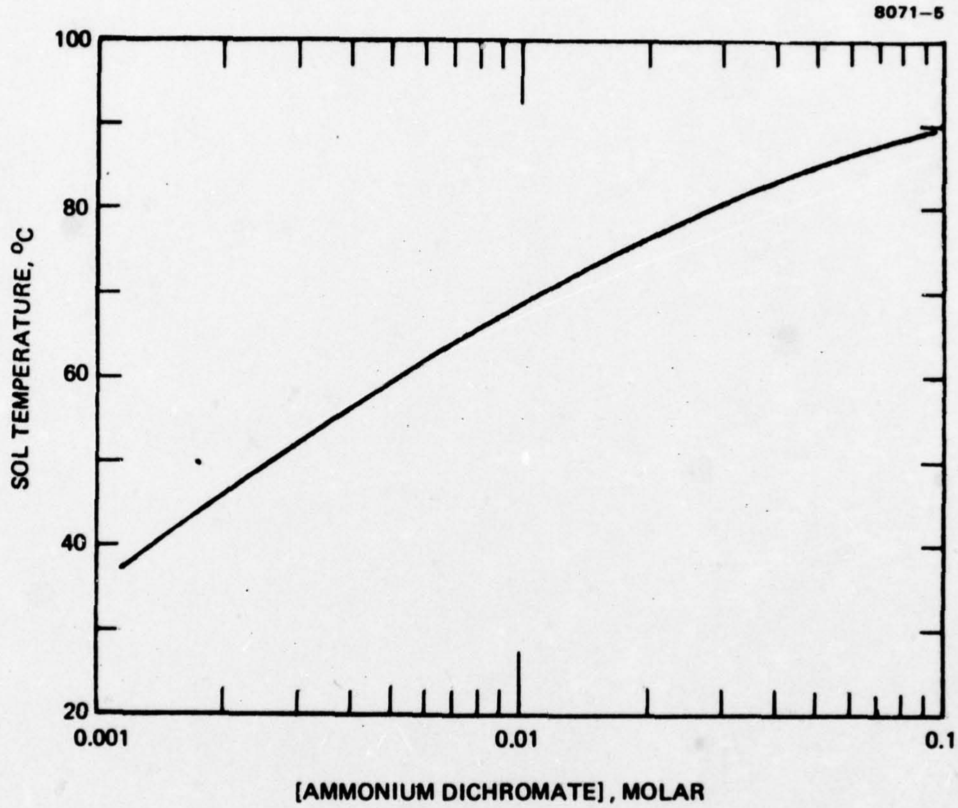


Figure 11. The sol temperature is an increasing function of ammonium dichromate in DCG films.

SECTION 5

FILM SWELLING CONTROL

The most important factor in the amplification of DCG index modulation is the film swelling achieved during the first development step. The swelling influences both the mechanical properties of the developed holographic film and the diffusion of dehydrating fluid into the grating structure. Internally, the film swelling is opposed by intermolecular cross-links, hydrogen bonds, and film crystallinity. Externally, film swelling is a function of several factors such as solution chemical composition, temperature, and pH. This section examines ways in which this swelling can be controlled to maximize index modulation.

A. pH EFFECTS

The relationship between gelatin swelling and pH can be understood by considering the amphoteric nature of gelatin. Water tends to flow into gelatin because of the ordinary thermodynamic tendency toward dilution. If the gelatin has a net charge, it will have a concentration of mobile ions associated with it. As in the Donnan membrane equilibrium, these will create a greater effective salt concentration inside the gel than outside and will increase the tendency of water to flow into the gel. However, as the network swells, chains between cross-links will assume elongated configurations and swelling will cease when elastic retractive forces equal the tendency to swell. One would, therefore, expect swelling to be greater the higher the charge on the gelatin.[24] The most swelling is therefore observed at the extremes of pH, as shown in Figure 12. Additionally, the intermolecular hydrogen bonding decreases as the pH goes to extremes. For acid processed gelatin in the isoelectric range, pH = 7 to 9, the ionic charges on the gelatin are balanced and the concentration of mobile ions, as well as film swelling, is at a minimum.

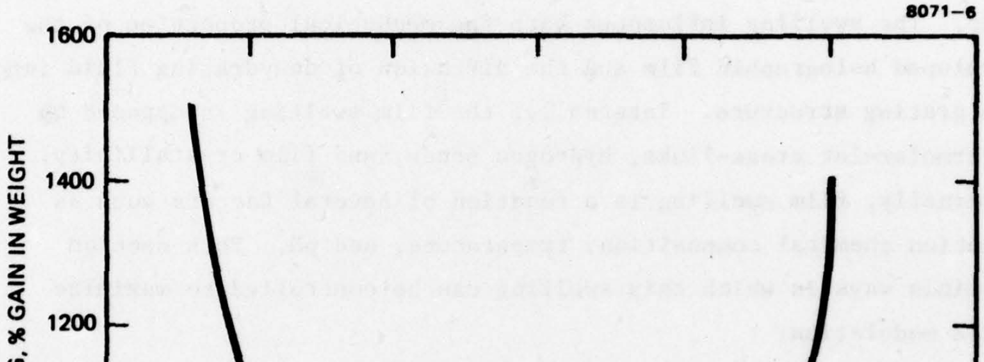


Figure 12. Gelatin film swelling in non-cross-linked materials is a strong function of pH.

We expected, then, that changes in development solution pH would affect the holographic properties of DCG holograms. We found that the reflection hologram wavelength bandwidth is a strong function of the pH of the DCG development water. In the broad mid-pH range, a low-noise, narrow-bandwidth image is generally obtained, as shown in Figure 13. At the extremes of pH, however, film swelling is increased markedly and cracking becomes predominant along with increases in spectral bandwidth. Concomitant with the appearance of these characteristics at very low and high pH is the appearance of scattering noise, particularly at the basic side. This dependence of holographic image quality on pH is related directly to film swelling,[25] as shown in Figure 13. At the extremes of pH, film swelling increases dramatically and is manifest in decreased film tensile strength and increased gelatin cracking. Although, from the point of view of strictly maximizing index modulation, the cracking mechanism may be preferred, the aggregate index modulation gives much narrower spectral bandwidths and lower scattering noise (see Section 8).

Development solution pH also affects the diffraction efficiency of DCG holograms. Figure 14 shows that diffraction efficiency is very high for acidic development solutions under a pH of 2, relatively constant in the mid-pH range from pH of 2 to about 12, and decreases rapidly to zero after a pH of 12. These results can again be interpreted in terms of film swelling dynamics and the two systems of image formation (see Section 8).

Below a pH of 2, the film swelling is very large, but not so large as to cause alcohol denaturation in the dehydration development step. The DCG film layer is so swollen that the tensile strength of the layer is lowered sufficiently to permit cracking along fringe boundaries. This also results in increased spectral bandwidth, as shown in Figure 13.

In the mid-pH range, the aggregate image is formed with decreased peak efficiency but also with narrowed spectral bandwidth. Film swelling is sufficiently large to permit the alcohol molecules to diffuse into

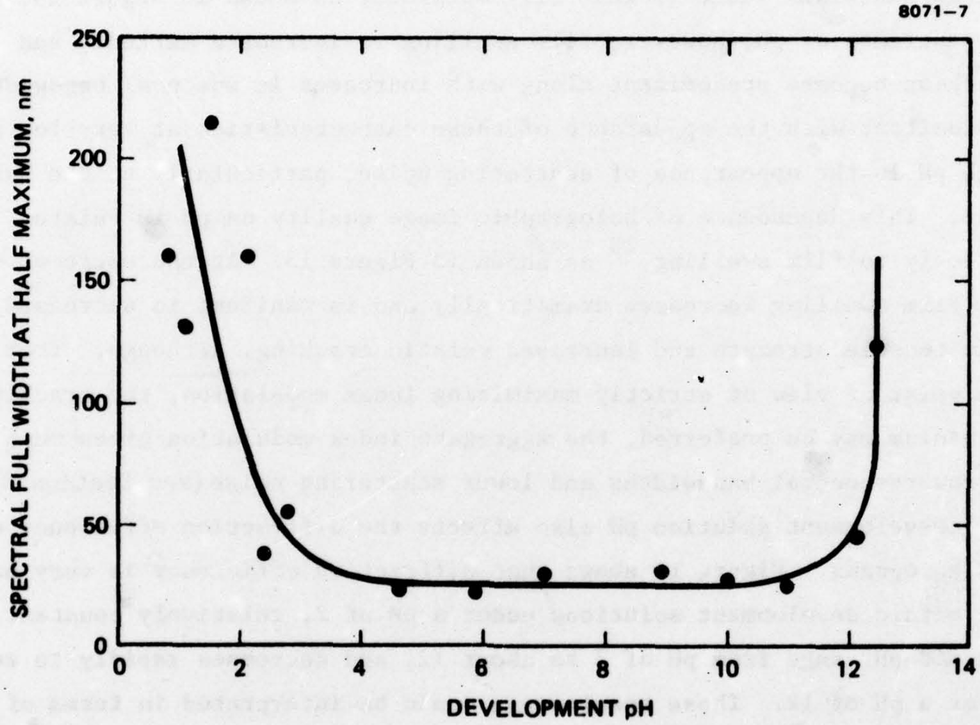


Figure 13. Dependence of spectral bandwidth in reflection holograms on the pH of the first development solution.

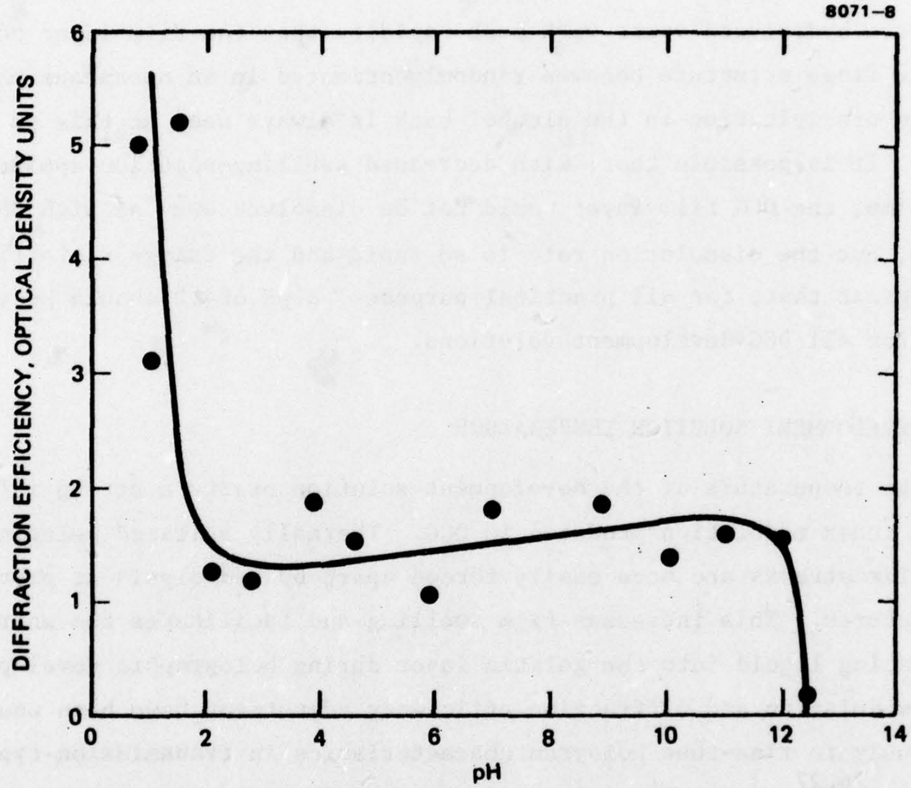


Figure 14. Light diffraction efficiency in reflection DCG holograms as a function of development water pH.

the gelatin layer. However, the gelatin cohesive forces are large enough in these pH ranges to restrain film cracking.

Above a pH of 12, the developing solution is sufficiently basic to cause complete breakdown of the gelatin matrix. The polypeptide molecules are hydrolyzed apart with such rapidity that the film layer holographic finge structure becomes randomly oriented in an amorphous mass. Gelatin precipitation in the alcohol bath is always seen at this pH range. It is possible that, with decreased swelling-solution application time, the DCG film layer would not be dissolved away at high pH values, but the dissolution rate is so rapid and the fringe distortion is so great that, for all practical purposes, a pH of 12 should be the limit for all DCG development solutions.

B. DEVELOPMENT SOLUTION TEMPERATURE

The temperature of the development solution exerts a strong influence on the index modulation produced in DCG. Thermally agitated gelatin molecular strands are more easily forced apart by hydrolysis at elevated temperatures. This increases film swelling and facilitates the entry of dehydrating liquid into the gelatin layer during holographic development. Index modulation and diffraction efficiency adjustment have been used previously to fine-tune hologram characteristics in transmission-type gratings.[26,27] Similar results are observed in reflection holograms within the aggregate image-formation mechanism (see Section 8).

Figure 15 shows the diffraction efficiency of reflection holograms as a function of holographic exposure energy at three different development solution temperatures (where A = 24°C, B = 22°C, and C = 20°C.). The holograms at all three temperatures contain only the aggregate image of index modulation; between 24 and 27°C, the cracking image begins to appear. The cracked image appears as a highly efficient hologram, as discussed in Section 8. Above 27°C, the cracked image predominates and the films begin to show signs of gelatin dissolution and precipatation in the alcohol baths.

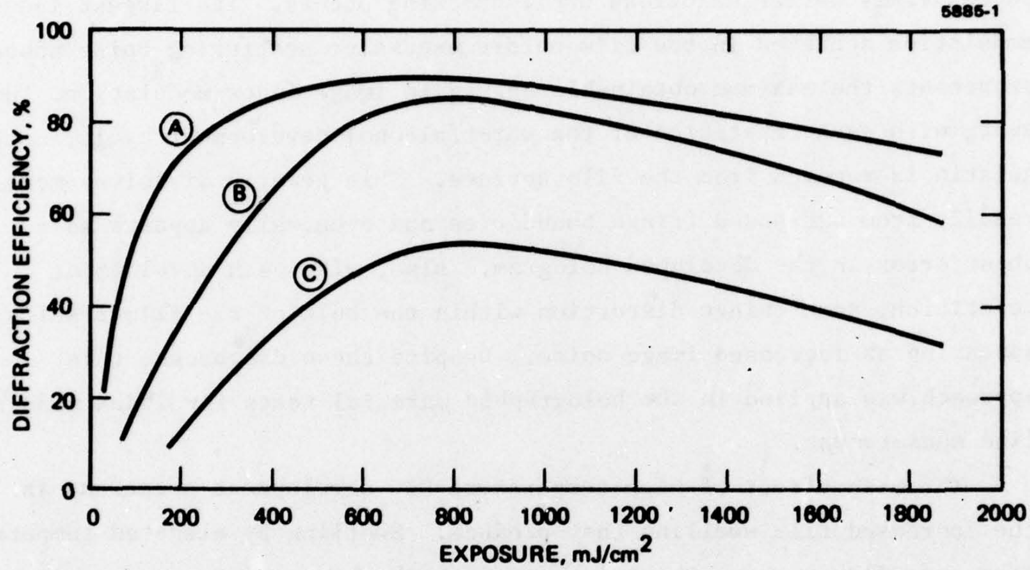


Figure 15. Light diffraction efficiency as a function of laser exposure energy at 514.5 nm for three development water temperatures.

This dependence of holographic properties on the temperature of the development solution can be used to evaluate DCG materials for maximum index modulation production capability. It is possible to take an exposed DCG film with a certain chemical treatment and develop it in successively warmer solutions until cracking occurs. The largest index modulation achieved in the film before excessive scattering noise appears represents the maximum obtainable aggregate image index modulation. However, with each repetition of the water/alcohol development cycle, some gelatin is removed from the film surface. This gelatin dissolves more readily from unexposed fringe boundaries and eventually appears as a phase error in the developed hologram. Also, with each development repetition, some fringe distortion within the bulk of the film results, appearing as increased image noise. Despite these drawbacks, this approach was applied in the holographic material tests for index modulation measurement.

The main effect of high-temperature DCG development solutions is the increased film swelling they produce. Swelling by elevated temperature generally acts on the holograms in much the same way as extremes of pH: first increased aggregate index modulation is observed, then film cracking, and finally film dissolution with gross gelatin precipitation in the alcohol bath.

A series of reflection holograms were developed at successively higher temperatures. Index modulation increased almost linearly with temperature, as shown in Figure 16. All other experimental variables (e.g., solute content, pH) were kept constant. At 30°C, the sol temperature was approached in these films; above this temperature, severe grating distortion occurred. Generally, each particular film preparation will have its own characteristic sol temperature and a correspondingly "destruct temperature" unique to the film hardness. Since finding the destruct temperature may take some initial trial-and-error experimentation in each case, it is impossible here to specify a particular

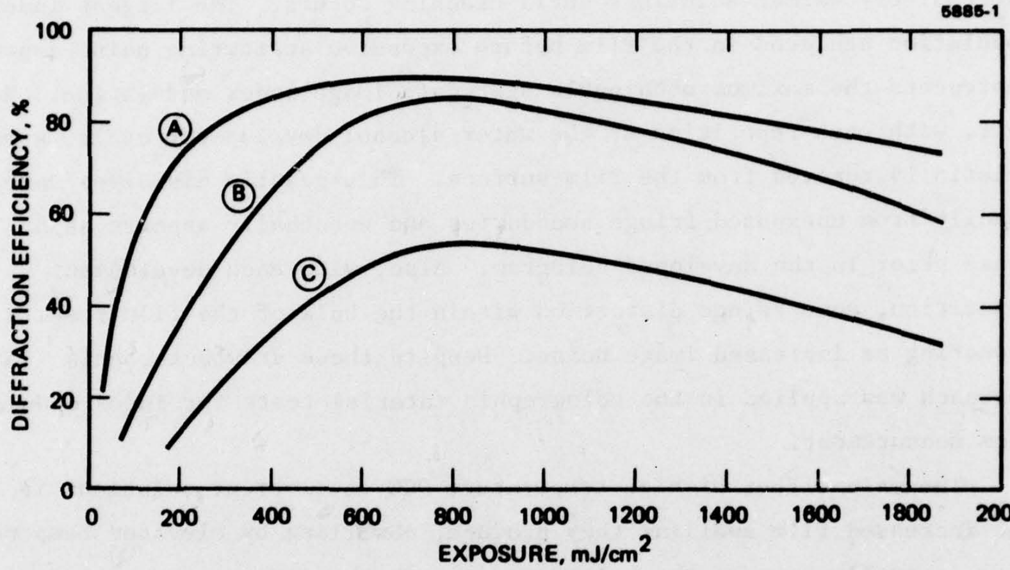


Figure 15. Light diffraction efficiency as a function of laser exposure energy at 514.5 nm for three development water temperatures.

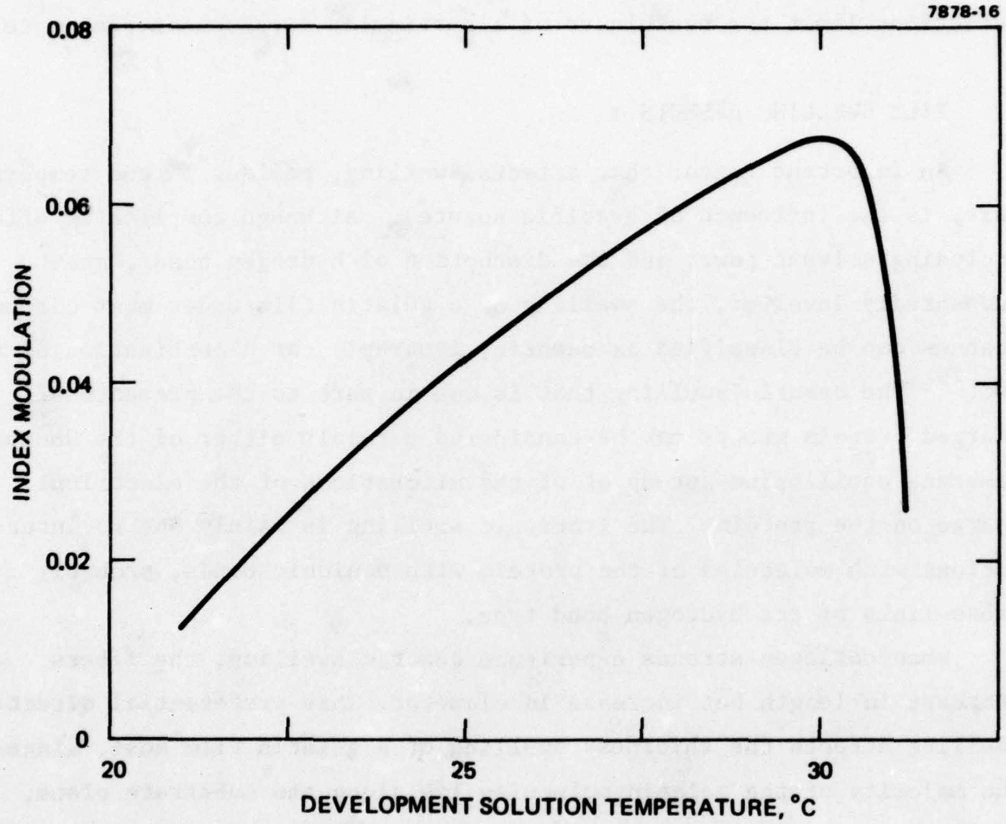


Figure 16. Optical index modulation in reflection holograms with increasing development solution temperature.

temperature for all holographic films. Even when the gelatin on commercial photographic plates is used, batch-to-batch film hardness variations limit the usefulness of a particular development procedure.[28]

C. FILM SWELLING EFFECTS

An important factor that affects swelling, besides pH and temperature, is the influence of specific solutes. Although complicated effects, including solvent power and the disruption of hydrogen bonds, are undoubtedly involved, the swelling of a gelatin film under most circumstances can be classified as osmotic, lyotropic, or a combination of the two.[29] The osmotic swelling that is due in part to the presence of charged protein groups may be considered a result either of the Donnan membrane equilibrium set-up or of the alterations of the electrical charge on the protein. The lyotropic swelling is mainly due to interactions with molecules of the protein with nonionic bonds, probably cross-links of the hydrogen bond type.

When collagen strands experience osmotic swelling, the fibers decrease in length but increase in diameter. This preferential directional swelling affects the thickness swelling of a gelatin film most, since the majority of the gelatin molecules lie along the substrate plane, much like spaghetti lying on a table top. In lyotropic swelling, on the other hand, only the width of the film increases as a result of the lessened cohesion and the separation of the component fibrils.

In hologram development, the type of swelling that precedes alcohol dehydration determines the obtainable index modulation. Osmotic differs from lyotropic swelling in the way the molecular strands become separated, and the alcohol molecules are either facilitated or retarded in their diffusion into the bulk of the film.

When swelling-control compounds are applied to holographic DCG development, several factors must be considered. First, as the gelatin film is bathed in a salt solution, the salt will enter the gelatin layer as the water swells it. As the film is processed in the second development solution, the solubility of the salt in the second solution will determine the levels of light scattering noise produced. That is, if the salt (e.g., NaCl) has a low solubility in alcohol, then it will precipitate out of solution inside the gelatin film. The precipitated salt not only creates light scattering centers in the gelatin, but also facilitates gelatin precipitation and optical denaturation. Water solutions containing even small amounts of NaCl used for the first development bath show marked whitening in the developed holographic plate. The second consideration is what effect the solute will have on the swelling properties of the gelatin film. We know that solutes in general will osmotically retard the flow of water into the gelatin layer. Hence, increased solute concentrations will produce less swelling, which will result in less light diffraction efficiency and less index modulation. On the other hand, certain solutes will swell the gelatin lyotropically and tend to counterbalance, if not exceed, the osmotic swelling retardation. If the swelling is increased by a particular solute, then the index modulation should be improved by applying that solute. However, if a particular solute has too much solvent power for the gelatin, holographic fringe stability may be disrupted, resulting in decreased diffraction efficiency. A complicating factor is that these properties for each solute are probably dependent on several variables, such as concentration, pH, and temperature. For example, at very low concentrations, NaCl may not exceed its solubility limit in alcohol. Hence, additional scattering centers would not be formed at low NaCl concentrations. Additionally, since NaCl solution is not a very effective lyotropic swelling agent,[30] maximum index modulation would be gained at minimum concentrations. At a high salt content, film swelling would be retarded osmotically and minimum index modulation would result. With these interrelated effects in mind, we selected several solutes for further study.

Our first task was to evaluate solutes for their water and alcohol solubilities. We chose sodium iodide for its high water (184 g/100 ml) and alcohol (43 g/100 ml) solubilities from the sodium, potassium, ammonium, and calcium halide salts. Calcium nitrate was also selected for its high water (92 g/100 ml) and high alcohol solubilities. Sodium chloride was chosen as a control salt, having good water solubility but only slight solubility in alcohol. For the organic solutes, we chose trimethyllaurylammoniumchloride (TMLAC), glycerol, and triethanolamine since they are very soluble in both water and alcohol and are known to interact with the gelatin molecular structure.[31]

Our next selection step was to determine which solutes can increase gelatin swelling more than the osmotic swelling is depressed by their presence. We decided to perform an indirect jelly strength (Bloom) test to determine each solute's ability to disrupt the formation of a solid gel. We measured the amount of weight, in grams, required to depress a 0.5-in.-diameter cylindrical post 4 mm into the surface of a gel that had been set for 16 hr at 5°C. To validate our measurement device, we first determined the Bloom rating of various gelatin concentration gels, as shown in Figure 17. As expected, increases in gelatin concentration were approximately linear with increased jelly strength for the range of values tested.

In the inorganic salt category, NaCl showed very little influence on jelly strength from a 0.01 to 1.0 molar concentration. This apparent inability to disrupt gelatin film integrity, coupled with its low solubility in alcohol, produced holograms of markedly increased light scattering and decreased index modulation. Although these two undesirable characteristics eliminate NaCl from consideration as a solute additive, they do point to the necessity of using relatively mineral-free water for washing DCG holograms. We did not determine the exact point at which excessive scattering or efficiency decrease took place, but it is suggested that, for improved repeatability of holographic development, some form of deionized or distilled water should be used. Both the calcium

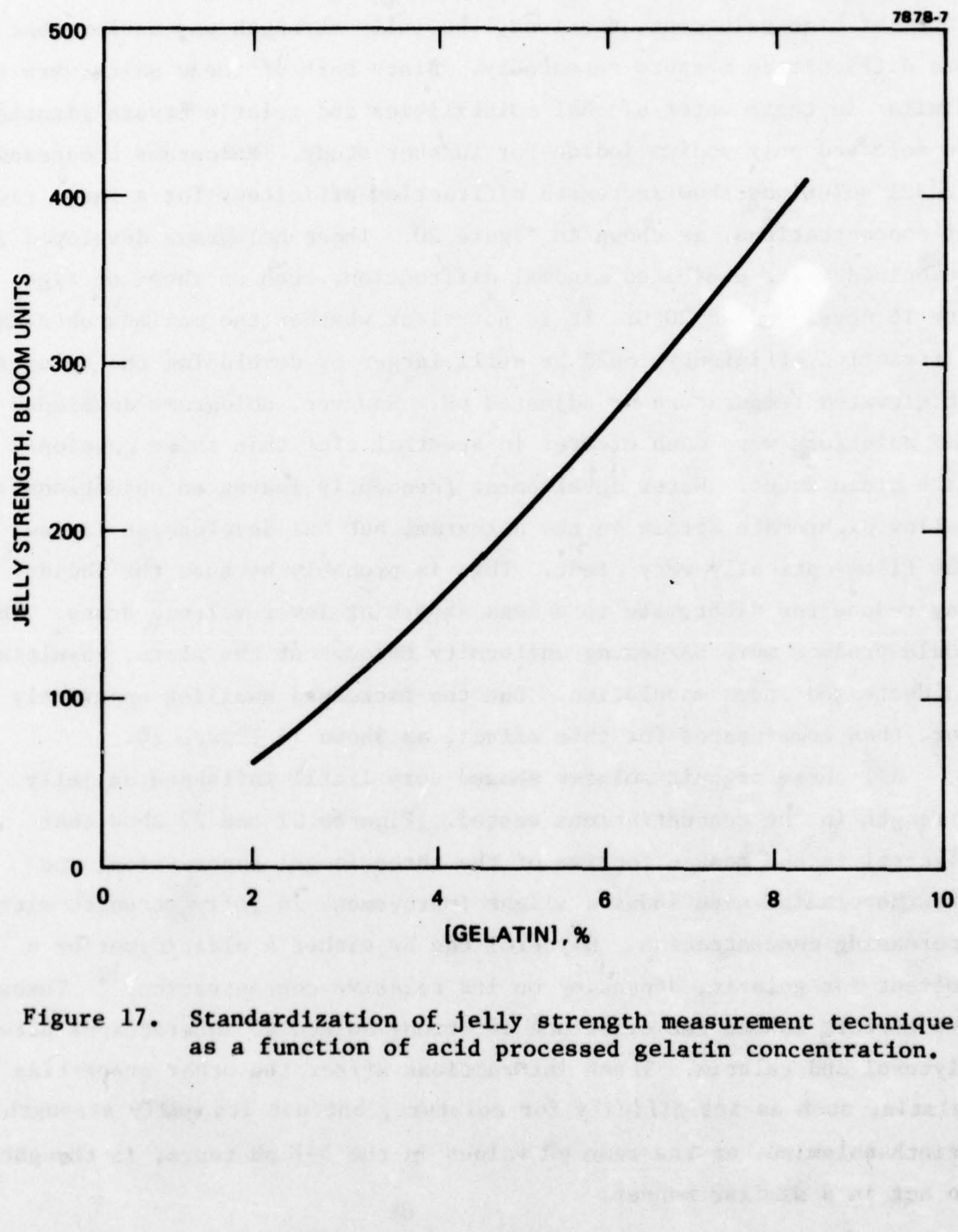


Figure 17. Standardization of jelly strength measurement technique as a function of acid processed gelatin concentration.

nitrate and sodium iodide salts exhibited a decrease in jelly strength when used in high concentrations, as shown in Figures 18 and 19. In fact, at high salt concentrations, the jelly strength was so low that it was difficult to measure repeatably. Since both of these salts were so similar in their water/alcohol solubilities and gelatin crystallization, we selected only sodium iodide for further study. Holograms processed in NaI solutions show increased diffraction efficiency for a large range of concentrations, as shown in Figure 20. These holograms developed in deionized water exhibited minimal diffraction, such as those of Figure 16 developed at 20°C. It is not clear whether the maximum obtainable diffraction efficiency could be still larger by developing the holograms at elevated temperature or adjusted pH. However, holograms developed in NaI solutions were much clearer in spectral tint than those developed with plain water. Water development frequently leaves an objectionable yellow dichromate strain in the hologram, but NaI development leaves the films optically very clear. This is probably because the iodide may reduce the dichromate to a less absorbing lower valence state. This would produce more hardening uniformity throughout the plate, resulting in decreased index modulation. But the increased swelling apparently more than compensates for this effect, as shown in Figure 20.

All three organic solutes showed very little influence on jelly strength in the concentrations tested. Figures 21 and 22 show that glycerol is the most effective of the three in gel suppression, and triethanolamine even shows a slight improvement in jelly strength with increasing concentration. Glycerol can be either a plasticizer or a solvent for gelatin, depending on its relative concentration.[32] These two effects denote the existence of strong molecular interactions between glycerol and gelatin. These interactions affect the other properties of gelatin, such as its affinity for moisture, but not its jelly strength. Triethanolamine, at the same pH values in the 5-7 pH range, is thought to act in a similar manner.

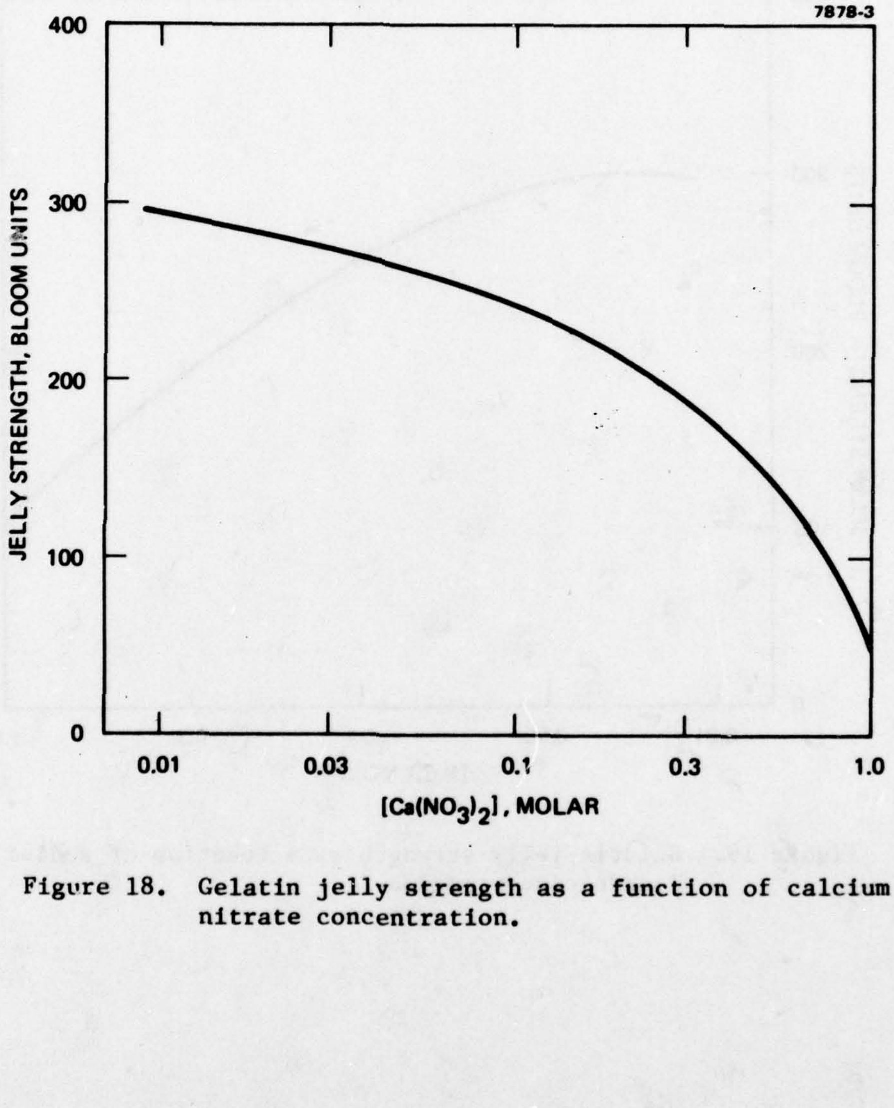


Figure 18. Gelatin jelly strength as a function of calcium nitrate concentration.

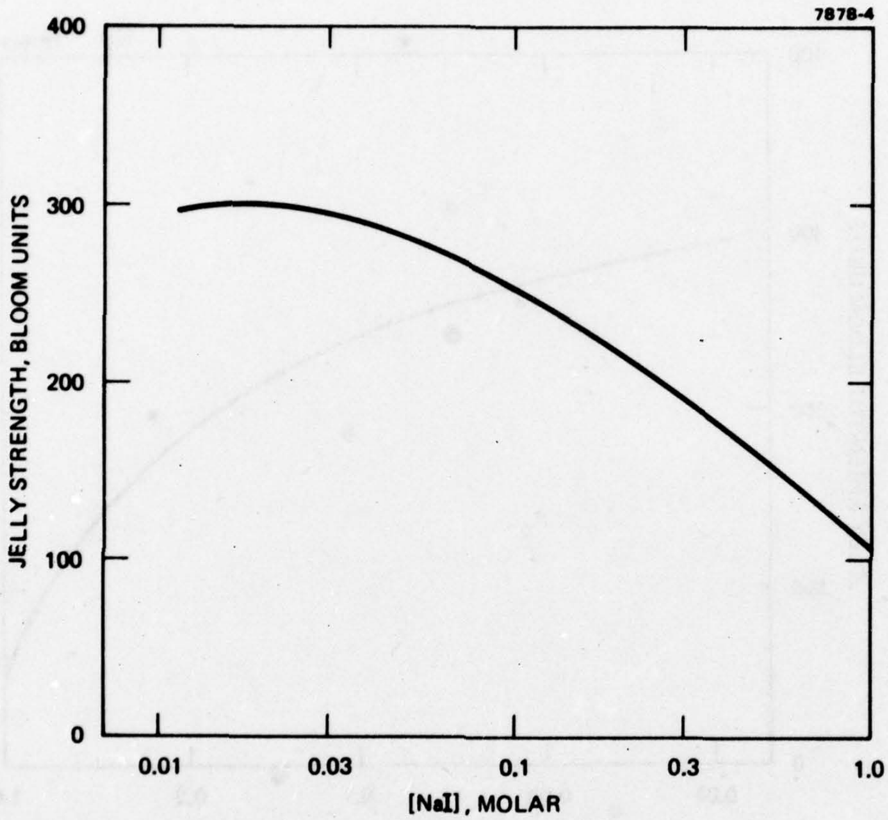


Figure 19. Gelatin jelly strength as a function of sodium iodide concentration.

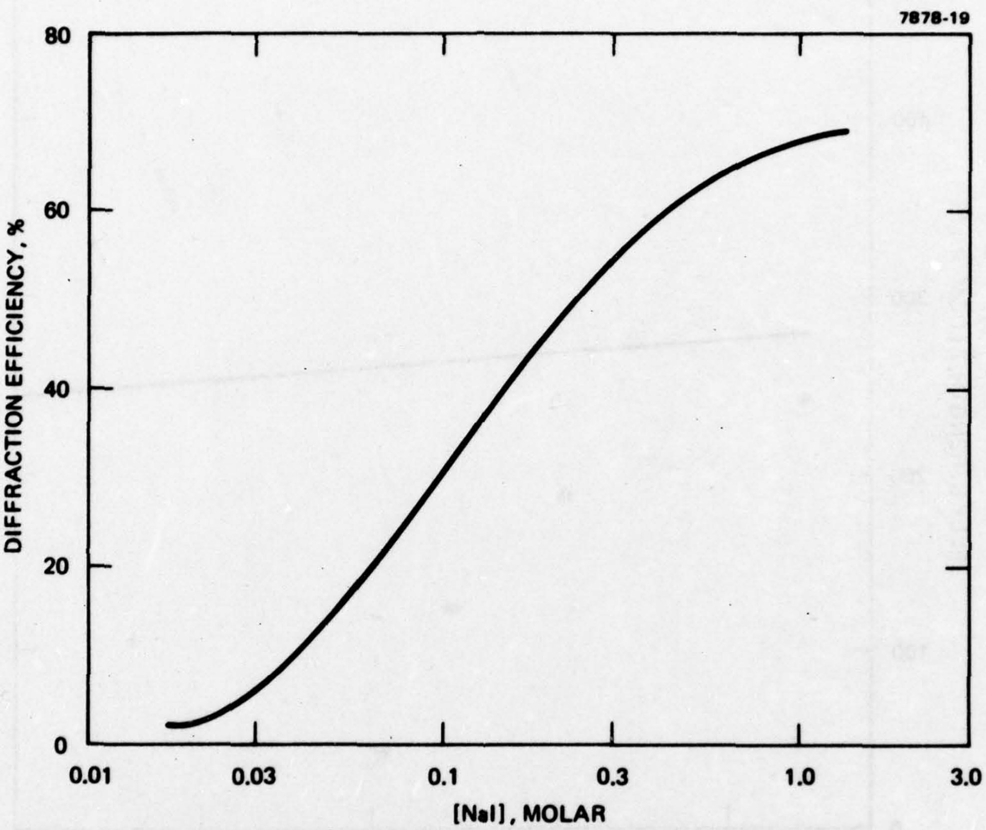


Figure 20. Light diffraction efficiency can be substantially improved with sodium iodide addition in the development bath.

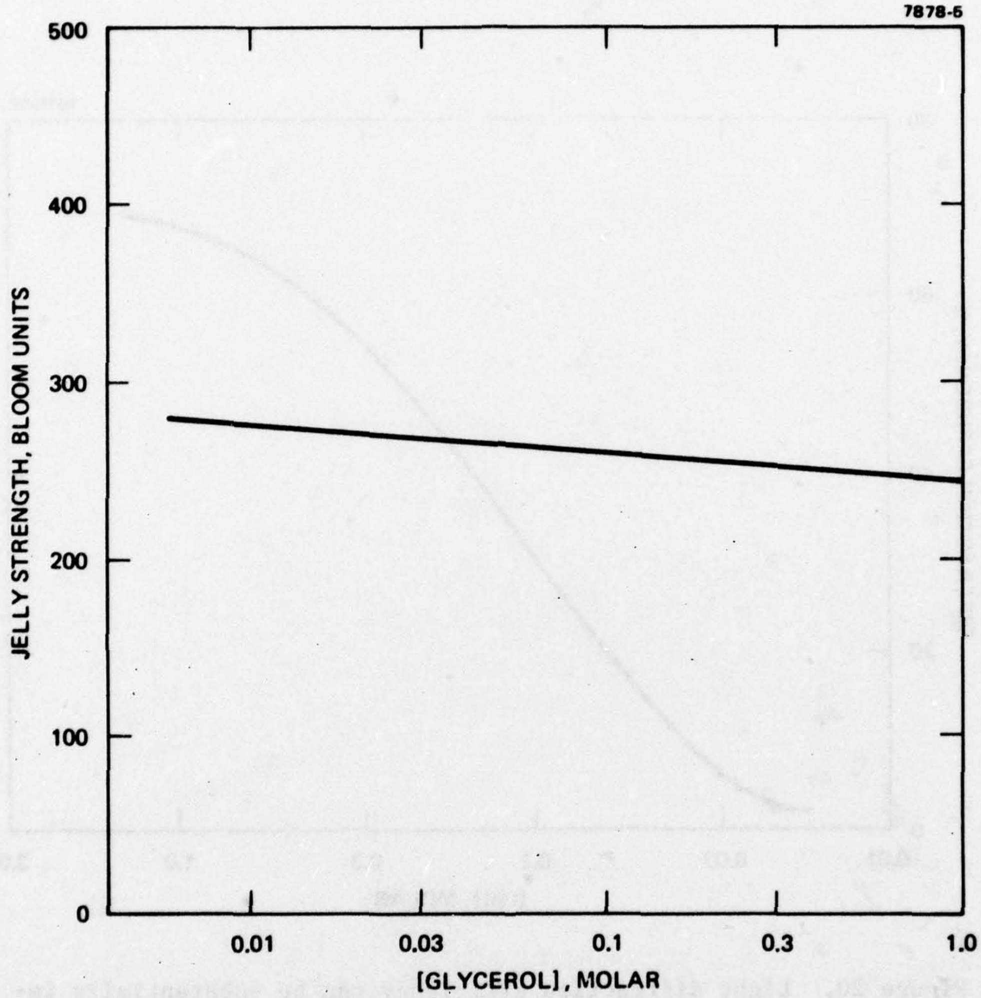


Figure 21. Gelatin jelly strength as a function of glycerol concentration in the gel.

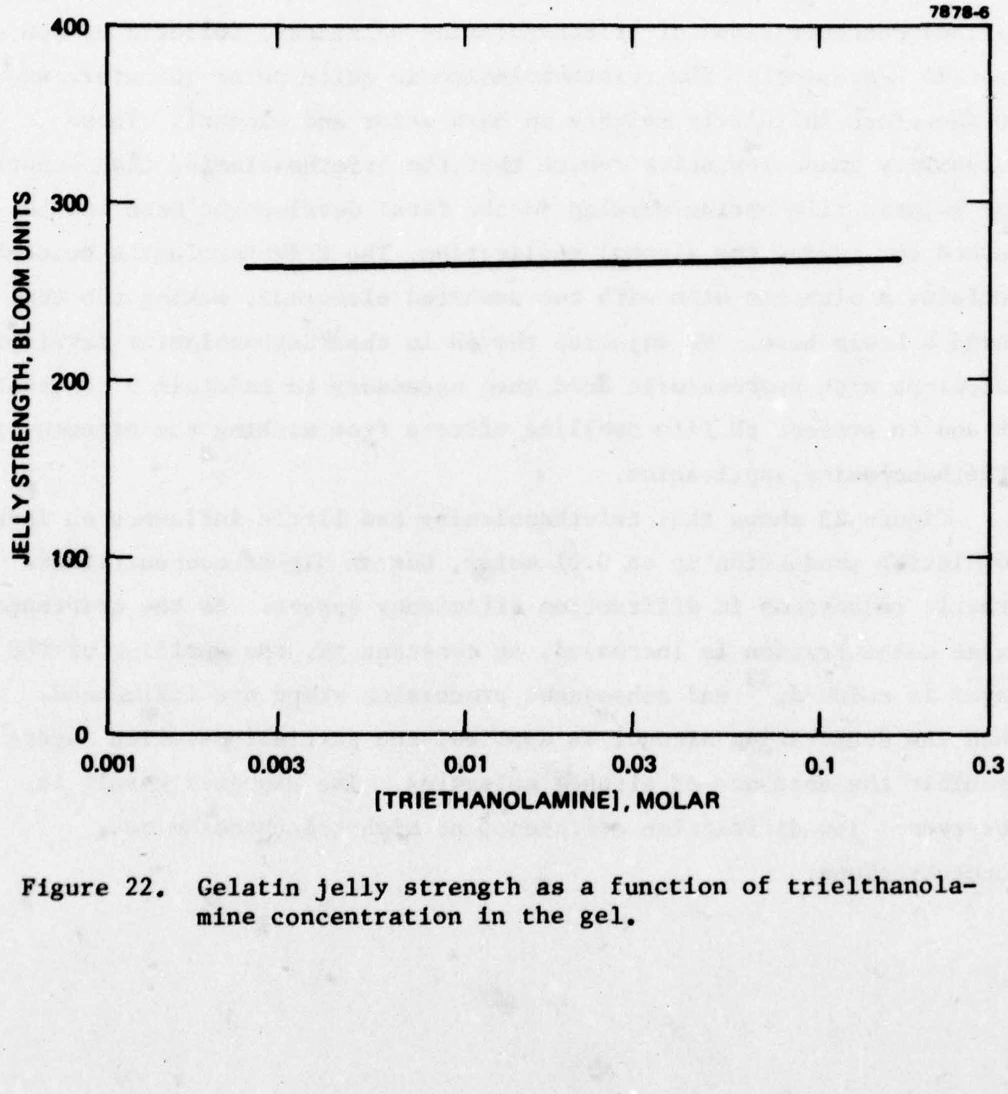


Figure 22. Gelatin jelly strength as a function of trielthanolamine concentration in the gel.

We investigated holographic properties produced by the swelling control of gelatin films with the multi-functional organic compound triethanolamine. Reflection holograms recorded in DCG were developed in various concentrations of triethanolamine solutions, followed by dehydration in 2-propanol. The triethanolamine is quite polar in nature and is therefore infinitely soluble in both water and alcohol. These solubility characteristics ensure that the triethanolamine that penetrates the gelatin film during soaking in the first development bath can be washed out during the alcohol application. The triethanolamine molecule contains a nitrogen atom with two unshared electrons, making the compound a Lewis base. We adjusted the pH in the triethanolamine developing solutions with hydrochloric acid when necessary to maintain a constant pH and to prevent pH film swelling effects from masking the effects of triethanolamine application.

Figure 23 shows that triethanolamine has little influence on index modulation production up to 0.01 molar, but at higher concentrations drastic reductions in diffraction efficiency appear. As the triethanolamine concentration is increased, at constant pH, the swelling of the layer is reduced,[33] and subsequent processing steps are influenced. When the dehydrating alcohol is applied, the partially swollen layers prohibit the entrance of alcohol molecules. The expected result is observed: low diffraction efficiency at high triethanolamine concentrations.

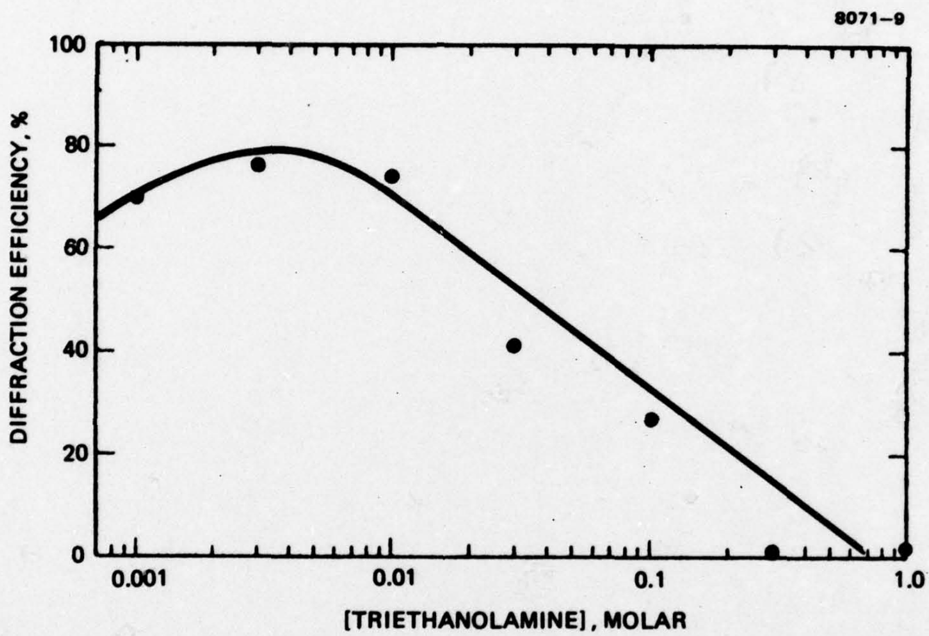


Figure 23. Example of osmotic swelling control of gelatin films by an organic compound, triethanolamine.

SECTION 6

SCATTERING NOISE SUPPRESSION

The major source of scattering noise in DCG films is the "precipitation" of gelatin in the alcohol development bath.[19] When a clear solution of gelatin is added to alcohol, the gelatin precipitates into a white amorphous mass. Similarly, when a gelatin film is swollen in water, there is usually more water than gelatin in the film; when it is then immersed in alcohol, the swollen film behaves as would a solution of gelatin, and a white precipitate is formed throughout the film. The rigidity of the film (i.e., amount of crystallinity and cross-linking) is the counterbalancing force that opposes the precipitation. Films that contain large gelatin crystals or that are highly cross-linked offer a high resistance to precipitation. It is believed that, on the molecular level in water-swollen films, a sheath of water surrounds individual gelatin molecules. Immersion into an alcohol solution causes the water to be withdrawn from the layer with hydrogen bond disruption, and the gelatin molecules undergo conformational changes. If these changes are large or fast enough, the gelatin becomes "optically denatured" by forming scattering centers.[34,35]

A. GELATIN OPTICAL DENATURATION

Much of the effort in this program was devoted to studying scattering center formation in gelatin/alcohol/water solute systems. From these studies, we gained considerable insight into the chemical mechanisms and variables that influence scattering noise formation. Except for the few cross-links that exist in DCG films, swollen gelatin films are chemically practically indistinguishable from gelatin solutions in many ways. Both systems contain a small amount of gelatin dispersed or loosely held together in an aqueous base. Since gelatin solutions and swollen gelatin films are thought to be similar in their alcohol precipitation behavior, it is possible to apply gelatin solution precipitation data to noise formation in DCG films. An added advantage to this approach is that the operational parameters of pH, concentration, and chemical mixing are more easily defined in the gelatin solution than for swollen films.

Most proteins are denatured over a fairly sharp transition region by many organic solvents that are miscible with water.[35] Gelatin also exhibits this behavior in aqueous solutions when titrated with alcohol. The sharpness of the transition is illustrated in Figure 24. In less than a 2% alcohol concentration differential, gelatin dissolved in water turns from optically clear to densely scattering. (We use the words denatured and precipitated synonymously for optical scatter center formation in gelatin.) In this respect, biological materials, such as gelatin, are remarkably specific in their solubility characteristics. The sharpness of the precipitation point benefits the delineation of the solubility limits. The reaction is reversible, returning the solution to a clear state as water is added.

More quantitatively, Figure 25 shows the precipitation boundary in an alcohol/gelatin/water solution. Very weak gelatin solutions are hard to precipitate with alcohol, and more concentrated solutions appear to approach a limit at about a 50% alcohol concentration. This means that in holographic development the initial immersion of a water-swollen film will not cause scatter center formation. Once the film begins to osmotically collapse, its water content decreases, its alcohol content increases, and its tendency toward precipitation is increased. In fact, if the film swelling is, for example, five times larger than its dry thickness (equivalent to a 20% gelatin solution in Figure 24), then any alcohol concentration larger than about 53% inside the film will cause scattering noise formation. Our mission in the suppression of scattering noise is to find chemical techniques to improve the alcohol precipitation properties.

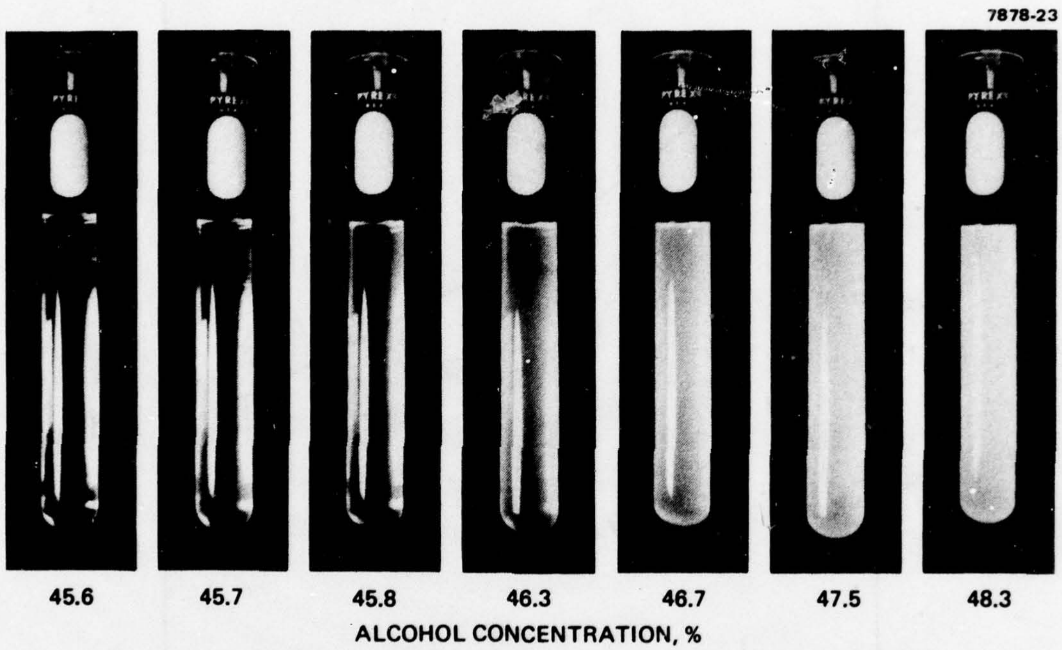


Figure 24. Denatured gelatin scattering centers appear over a sharp transition region with increasing alcohol concentration.

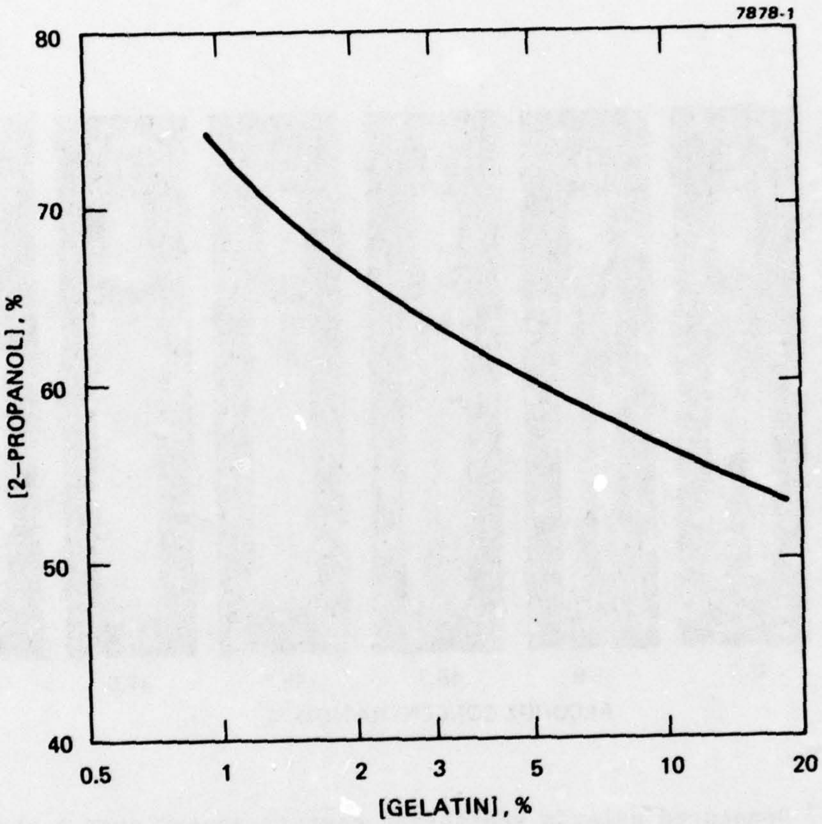


Figure 25. Minimum alcohol concentration required to precipitate gelatin from aqueous solution.

B. MOLECULAR WEIGHT AND DENATURATION

The minimum concentration of alcohol that is required to precipitate a gelatin solution can be used as a measure of the ability of gelatin to resist optical denaturation in that particular solution environment. The solubility of gelatin depends on the pH of the solution, the temperature, the concentration of other electrolytes present, and the composition of substances that may form a complex with gelatin, such as detergents.

Another important variable that affects the precipitation of gelatin solutions in alcohol is the composition of the gelatin itself. Although the amino acid composition of gelatin from many animals is known,[36] the molecular weight or the way the amino acids are coupled can vary substantially. Gelatin is extracted from animal parts in a series of "cooks," or batches, each cook being at a progressively higher temperature than the previous cook. The result of this extraction method is that the first cooks contain the higher molecular weight gelatin and have a correspondingly higher gel strength or Bloom rating.

We investigated the alcohol precipitation of gelatin with molecular weight or Bloom strength as a variable. By titrating gelatin sols with alcohol, we found that the concentration at which alcohol precipitates gelatin is clearly indicated by the sudden appearance of a cloudy, white precipitate. Figure 26 shows that, when a gelatin solution is heated for extended periods of time at high temperature, the alcohol precipitation concentration increases only slightly. The high temperature heating causes the gelatin to hydrolyze to lower molecular weight species. The precipitation concentration changes only about 1% in over 2 hr of substantial gelatin hydrolysis at 85°C. These results are in direct disagreement with predictions and tests made by previous investigators.[37] Our results show that molecular weight does not substantially affect alcohol precipitation of the gelatin sol.

To further confirm the apparent independence of molecular weight and precipitation concentration, we tested a series of gelatins having

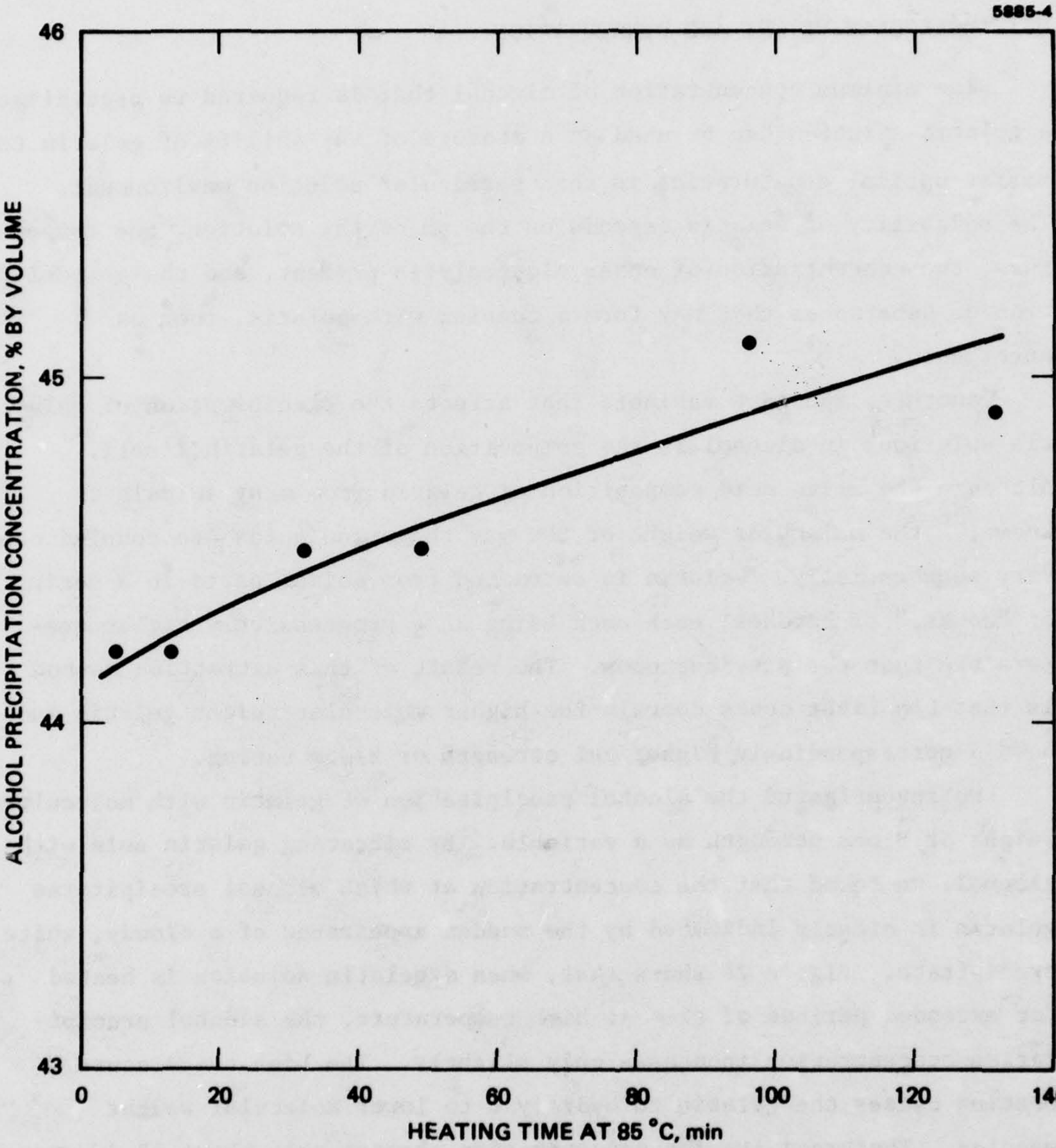


Figure 26. Alcohol concentration at the point of gelatin sol precipitation as a function of solution heating time.

the same animal source (porkskin), method of extraction (acid), and conditions of processing (except for the Bloom strength). Figure 27 shows that low-Bloom gelatins, up to 250 Bloom strength, precipitate in about 45% alcohol solutions. Above 250 Bloom strength, the gelatin is considerably more resistant to alcohol precipitation. However, there is an apparent inconsistency in these data. The data in Figure 26 shows that the alcohol precipitation concentration is higher for lower-molecular-weight gelatin, while Figure 27 seems to indicate the opposite. This apparent contradiction can be explained in terms of how the two gelatin precipitation tests were made. In Figure 26, a particular gelatin was degraded with heat, whereas in Figure 27 different Bloom-strength gelatins were extracted from the same animal hides. The first high-Bloom extraction cooks from the hides take out gelatin that is younger and not yet completely incorporated into the hide tissue. Hence, it not only differs in molecular weight from higher-temperature cooks, but also has a different solubility characteristic. The solubility characteristics and adhesion properties of high-Bloom gelatin indicate that it is much more hydrophobic than its low-Bloom counterparts. This hydrophobic nature apparently makes it more compatible to the more-hydrophobic alcohol environment that it encounters in holographic development.

C. pH AND DENATURATION

Because of its ionizable groups, gelatin can be classified as an amphoteric substance, capable of being titrated by either acid or alkali. The acidic groups in gelatin are the aspartic and glutamic acids and the terminal carboxyl acid groups; the basic parts are supplied as Lewis bases in histidine, lysine, arginine, and the terminal amino groups.[38] Since the ionization constants of these groups differ from each other, gelatin acts as a buffer for a large range of pH values, and correspondingly the population density of the various ionizable groups

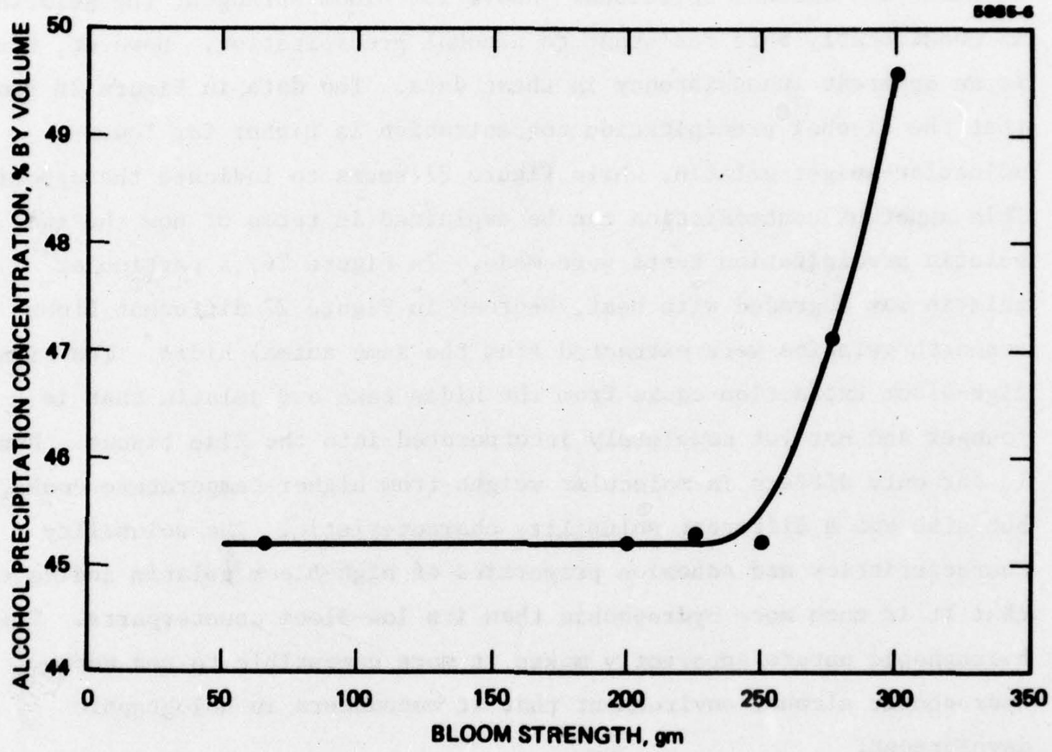


Figure 27. Alcohol concentration at the point of gelatin sol precipitation as a function of acid processed gelatin Bloom rating.

varies with the pH. Concomitant with the ionizable group changes, gelatin shows solubility changes in various solvents.

In an acidic solution, the gelatin molecules are positively charged by protonation and will migrate as a cation in an electric field. Alkaline solutions have the opposite effect, negatively charging gelatin, and it will migrate as an anion in an electric field. The intermediate point where the net gelatin charge is zero and no movement occurs in an electric field is known as the isoelectric point and is designated in pH units. Interestingly enough, gelatin shows a minimum of water solubility at the isoelectric point. Gelatin solutions often develop a concomitant turbidity that reaches the maximum at the isoelectric point.

We tested, as a function of the solution pH, gelatin precipitation characteristics in alcohol solutions that would be encountered in DCG hologram development. Type A gelatin, having a broad isoelectric region between about pH 7 and 9, was used in these precipitation tests. The alcohol precipitation concentration was operationally defined as that concentration at which a gelatin solution will visually sustain a turbid precipitate.

Figure 28 shows that gelatin is most susceptible to precipitation, and hence to optical noise formation, near its isoelectric point at pH 7. A comparison with Figure 12 reveals that the alcohol precipitation minimum has a much narrower pH range than the pH region for aggregate image formation, which extends roughly from pH 3 to 11. This implies that, for a minimum of noise formation in DCG holographic recordings, the pH of the developing water or swelling solution should be adjusted away from the isoelectric point, but not so far as to initiate film cracking at the extremes of pH.

The optical turbidity that is observed with alcohol precipitation is a reversible phenomenon, much like the scattering noise that appears on DCG holograms that receive insufficient prehardening. The reversal can be made by applying more water to the turbidity, but this is not

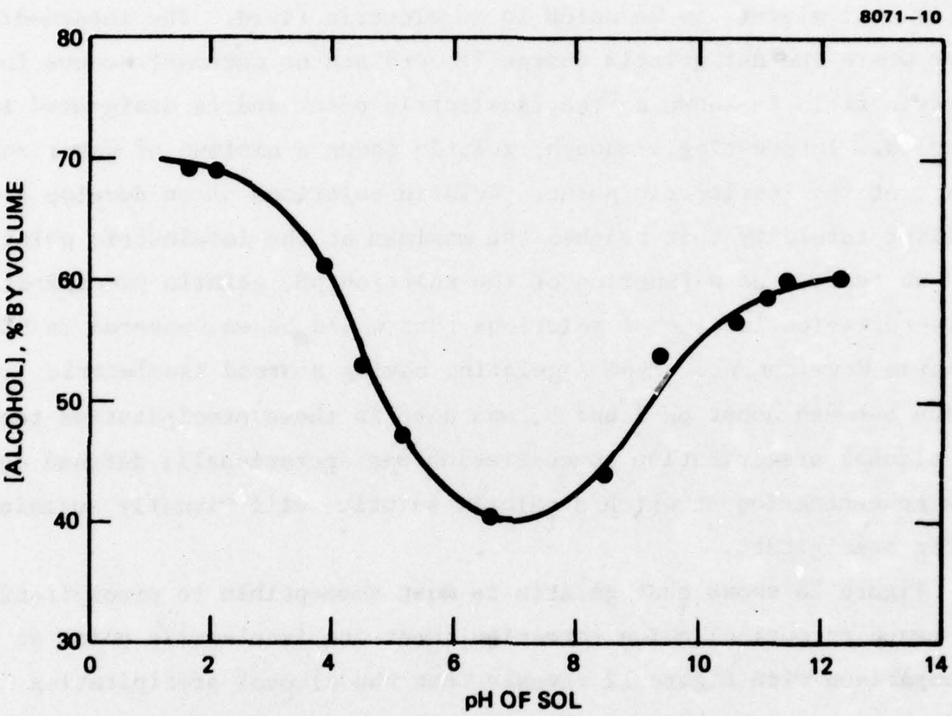


Figure 28. Minimum concentration of isopropyl alcohol needed to precipitate acid-processed gelatin as a function of pH.

practical in the developed DCG hologram since the image disappears with water application. Prevention of the initial optical noise formation appears to be the only choice.

D. SALT SOLUTIONS AND DENATURATION

Proteins often change their solubility characteristics in aqueous solutions when neutral salts are present. The effect of salts in increasing the solubility is called the "salting in" effect. In the "salting out" pehnomenon, which is the opposite effect, proteins are precipitated from aqueous solution by a high concentration of neutral salts. The solubility of proteins is a function of both pH and ionic strength, which is equivalent to molarity for univalent ions. Figure 29 shows that, in water-alcohol solutions, sodium chloride salt has a salting-in effect up to about 2 molar, after which the salting-out effect takes over. The magnitude of the salting-in effect, however, is quite small. Solubility is increased from about 44% to a maximum of just over 50% alcohol concentration. This salting-in effect was tested at a pH of 6.4.

We also tested briefly the salting-in behavior of two other salts: potassium acetate and ammonium nitrate. Both of these salts have good solubility in both water and alcohol solutions. At a 1 molar concentration, the alcohol precipitation concentration for these salts was 50.9 and 51.8%, respectively. Our conclusion is that these salts also act to salt-in gelatin in about the same way as does sodium chloride.

E. SOLUTES, pH, AND DENATURATION

The effect of salts on protein denaturation is of particular interest because of the appliction of salting-in and salting-out methods to control light scatter. At low concentrations, the ions of neutral salts (those that do not cause pH change in aqueous solution) can be expected to shield the charged groups of gelatin and thus have an

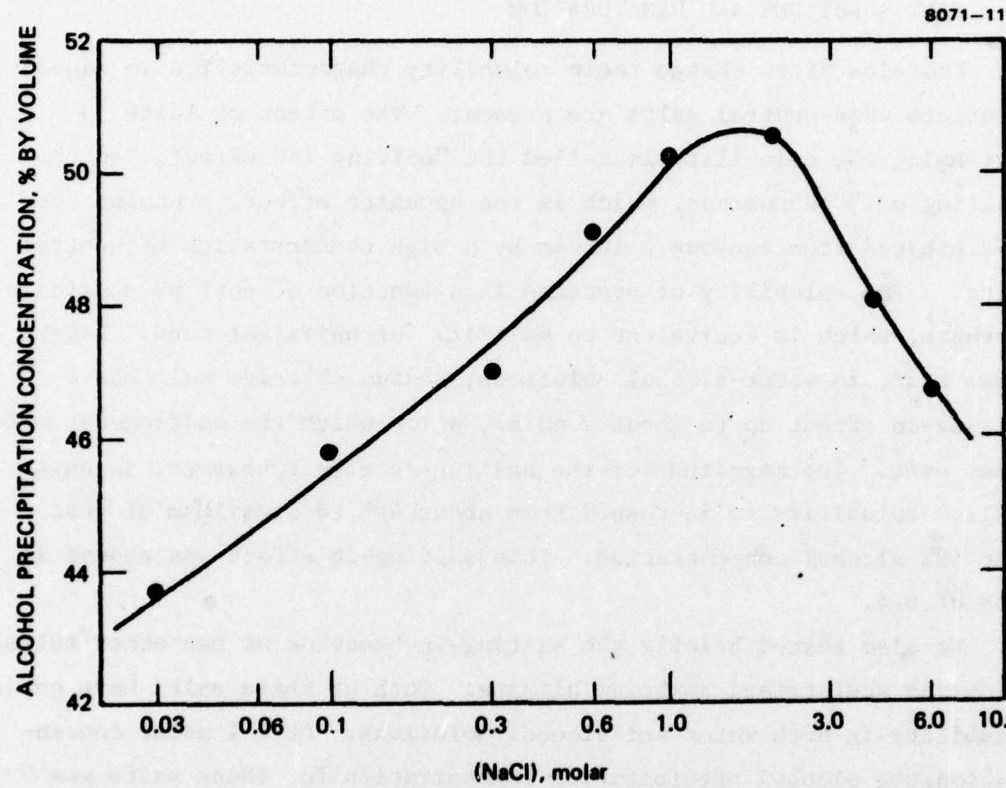


Figure 29. Minimum concentration of isopropyl alcohol needed to precipitate acid-processed gelatin as a function of solution salt concentration.

effect on electrostatic interactions between these groups. Experimental data have shown that the relative effectiveness of ions in stabilizing native proteins against conformational changes is the same as that noted in related processes, such as the stabilization of nucleic acids and the salting out of proteins. Thus, stabilizing action follows the classicial Hofmeister series that ranks the effectiveness of ions in salting out proteins.[39] A ranking for collagen/gelatin of the relative effectiveness of various ions promoting salting out and salting in is:

$$SO_4^{2-} < CH_3COO^- < Cl^- < Br^- < NO_3^- < I^- < CNS^- < (CH_3)_4N^+$$

$$< NH_4^+ < Rb^+, K^+, Na^+, Cs^+ < Li^+ < Mg^{2+} < Ca^{2+} < Ba^{2+}$$

$$< (C_2H_5)_4N^+ < (C_3H_7)_4N^+ .$$

The stability of proteins in aqueous salt solutions is further complicated with pH and organic solvent interactions. The relative applicability of the Hofmeister series to gelatins in water/alcohol/solute mixtures is difficult to determine a priori. Optical scattering noise measurements were made in a series of titrations. The three variables of solute composition, concentration, and pH were crossed to yield a series of precipitation curves for acid-processed gelatin, as shown in Figures 30 through 34. All of the plots of alcohol precipitation as a function of pH generally show the same type of response. In the isoelectric pH range (6 to 8), solubility is the lowest and scattering centers are easily formed with low alcohol concentrations. In this pH region, salting-in predominates despite the specific ranking of the solute on the Hofmeister series. The exception is TMLAC (Figure 34), which shows a slight salting out.

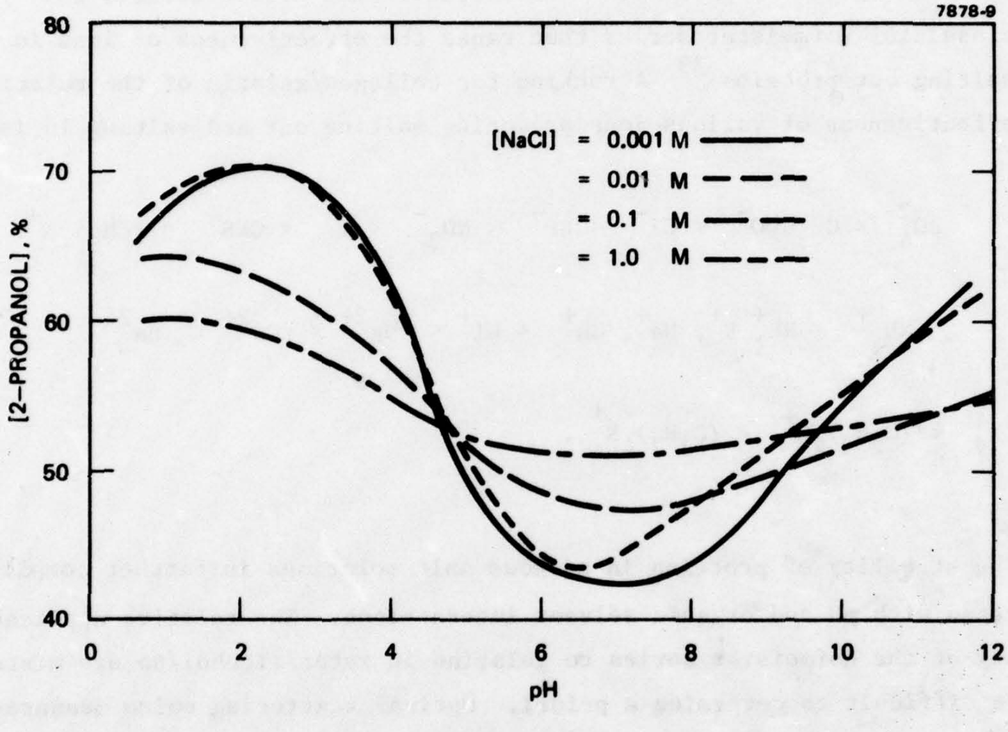


Figure 30. Alcohol precipitation of acid-processed gelatin sol as a function of pH and sodium chloride concentration.

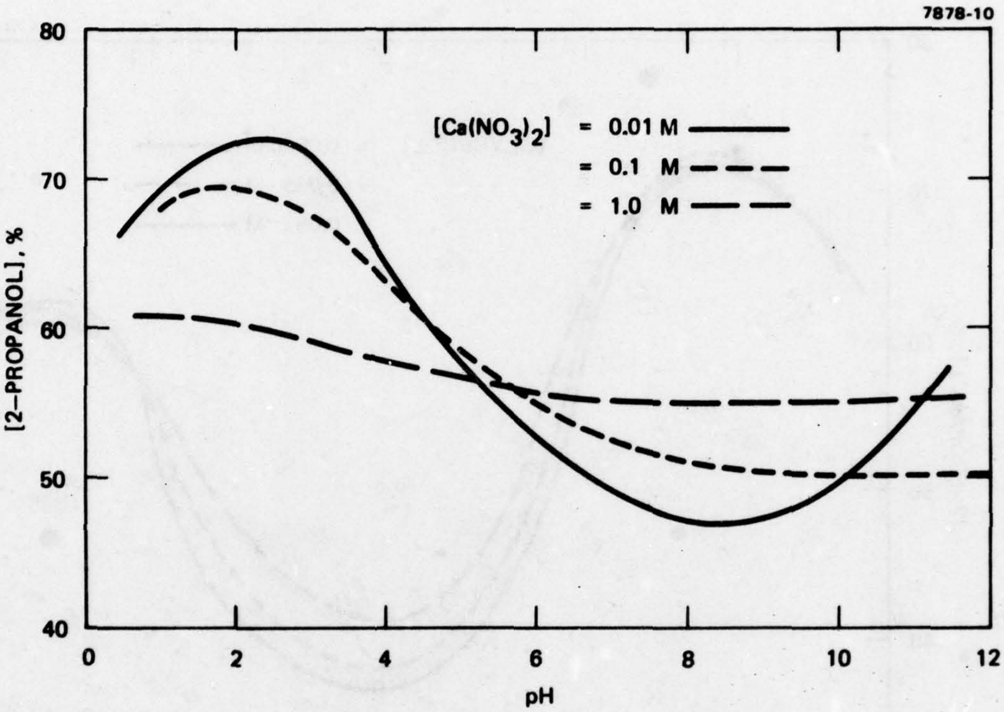


Figure 31. Alcohol precipitation of acid-processed gelatin sol as a function of pH and calcium nitrate concentration.

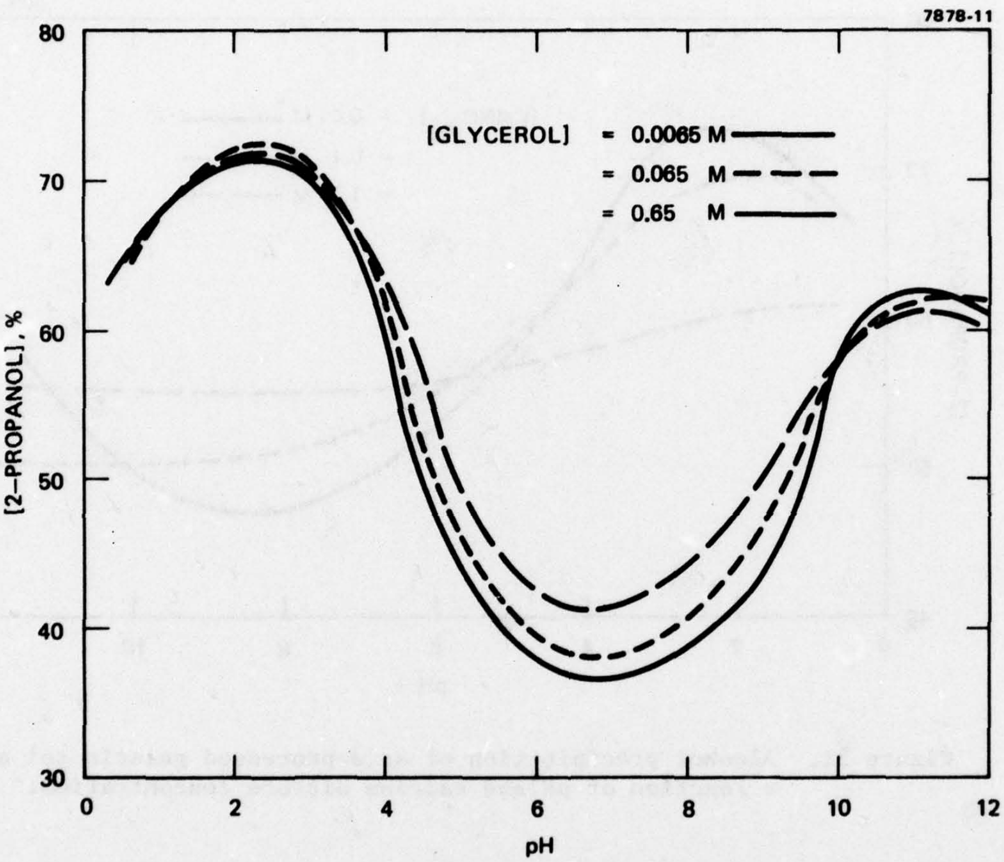


Figure 32. Alcohol precipitation of acid-processed gelatin sol as a function of pH and glycerol concentration.

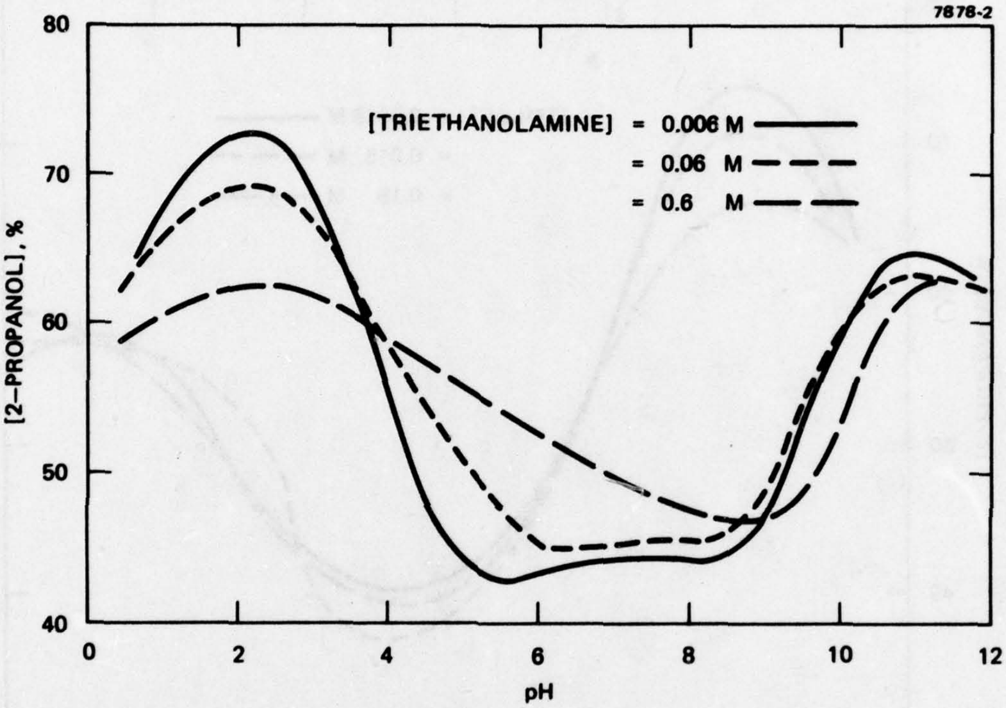


Figure 33. Alcohol precipitation of acid processed gelatin sol as a function of pH and triethanolamine concentration.

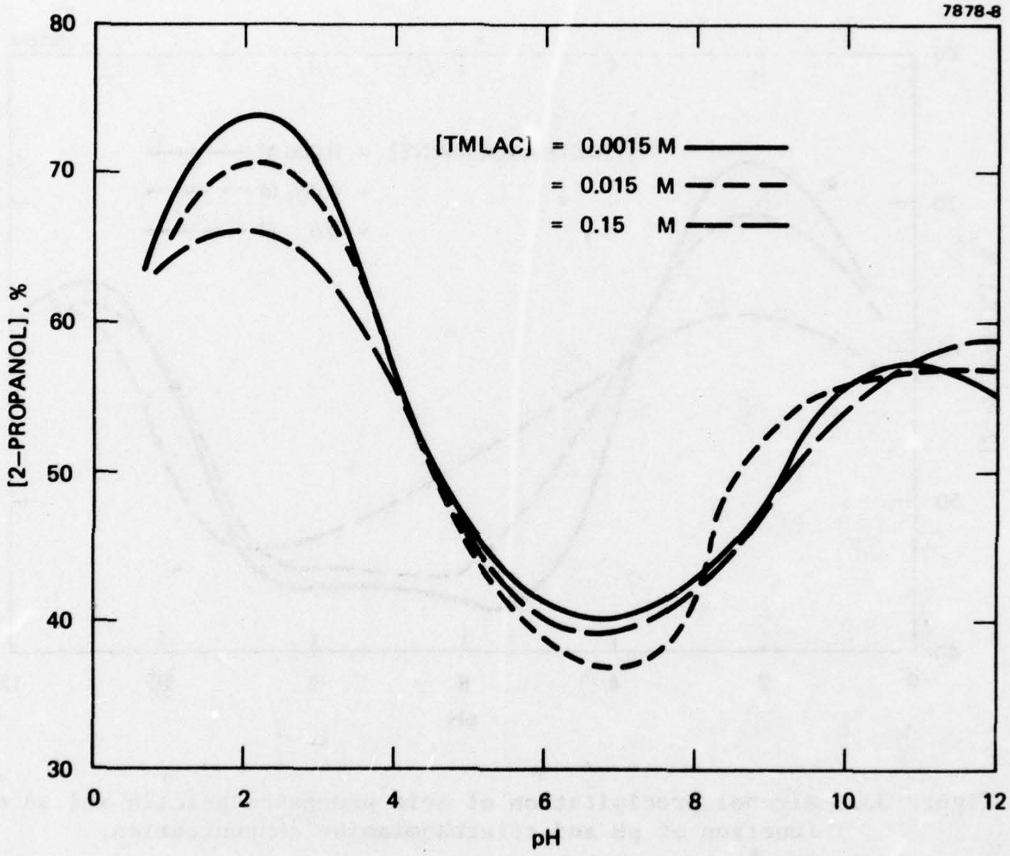


Figure 34. Alcohol precipitation of acid processed gelatin sol as a function of pH and trimethyllaurylammonium chloride.

In general, solutes appear to affect gelatin solubility in alcohol in one of two ways. In the first, we observe an appreciable solubility increase near the isoelectric point and a considerable decrease below approximately a pH of 4 to 5, as shown in Figures 30, 31, and 33. The TEA will be present as TEA•HCL at low pH values and as TEA at high pH values. This accounts for the uniqueness of the TEA precipitation curves in Figure 33. High pH precipitation is less predictable, but generally favors a salting-out behavior in alcohol solutions. In the second, the solute has little effect on gelatin scatter center formation when titrated with alcohol, as shown in Figures 32 and 34. Particularly, the presence of glycerol and TMLAC results in little solubility improvement.

The most important characteristic of a detergent, for our purposes, is that one end of the molecule is highly polar or ionic, whereas the remainder of the molecule is nonpolar or hydrocarbon-like. The polar end of the molecule tends to make it water soluble, while the nonpolar end tends to make it oil soluble. Concentrated alcohol and gelatin solutions, as oil and water, do not mix. However, when a small amount of oil and an aqueous detergent solution are shaken, an emulsion of the oil in the detergent solution is formed. The detergent molecules surround the fine oil droplets, their hydrocarbon "tails" being soluble in the oil. In a similar way, we expected the gelatin solubility to be altered when a detergent-protein complex is formed between gelatin and a detergent. This complex would present a mainly hydrocarbon surface to the more hydrocarbon-like alcohol. The solubility of the complex would be different from that of the gelatin molecule alone. Its relation to water as solvent would bear less relation to that of gelatin itself. We would expect, then, the presence of detergents to decrease the solubility of gelatin in water but increase its solubility in alcohol or some other more hydrophobic solvent.

We also examined briefly the use of a gelatin plasticizing agent, glycerol, in the hologram development process. The main effect of plasticizing agents such as glycerol in gelatin films is to block the hydrophilic functional groups,[32] similar to the action of detergents. The solvation of the gelatin hydrophilic groups by glycerol lowers their affinity for water. Simultaneously, the affinity for less polar solvents, such as alcohols, is increased. At high concentrations, glycerol is capable of suppressing index modulation formation in DCG holograms while also suppressing scattering noise formation.

The extensive binding of glycerol by gelatin polar side chains probably produces a strong solubilization effect. But the interactions with alcohol are more complicated since they almost certainly entail a strong solvation for the glycerol, regardless of the polarity of the side chains. The result is a gelatin precipitation behavior practically indistinguishable from that without glycerol.

When DCG holograms are developed in warm water solutions, index modulation increases up to a point, as shown in Figure 15, but film cracking is eventually encountered. We have found that the addition of surfactants, such as the TMLAC dissolved in the alcohol development bath, decreases the amount of film cracking and scattering noise formation at high temperatures. Low surfactant concentrations are effective in reducing some scattering noise, although the effect is small. For holographic DCG development, these results show that scattering noise suppression can be gained in the mid-pH range with specific solutes.[40] The effect of the neutral salts tested is to level the alcohol precipitation concentration across the entire pH range. That is, as the concentration of neutral salts is increased, the alcohol precipitation concentration approaches approximately 57% alcohol for all pH values. In none of the solutes tested could the alcohol precipitation concentration be improved beyond that delivered by a simple change in pH to the acid side. From the viewpoint of light scatter minimization, a pH of 2.5 appears optimum for holographic DCG film development. Figures 12 and 14 show, however, that high-diffraction-efficiency, wide-bandwidth images also begin to appear at these and lower pH values. Hence, before arbitrarily adjusting the pH of a DCG developing solution to 2.5, the gelatin film should contain a sufficient amount of prehardening or cross-linking to prevent excessive film swelling and crack image formation. Nakashima[41] advocates the use of a 0.7% HCl processing bath in DCG development following hardening with dichromate and a reducing agent. Assuming an assay of 37% in concentrated HCl and complete ionization of the acid in aqueous solutions, the acid developing bath calculates to a pH of 2.15, which is very close to our recommended pH value of 2.5 pH. Nakashima[41] claims a tenfold increase in film speed and a wide saturation region of diffraction efficiency (i.e., exposure latitude) for the acid processed holograms, although the chemical mechanisms are not made clear. We conclude that the appearance of these characteristics in holograms processed near pH 2.5 is due to the suppression of scattering noise formation since the precipitation of gelatin is the lowest in this pH region for a wide variety of added solutes. Reproducibility is also improved in acid processing of DCG holograms. At pH 2.5, small deviations in pH do not appreciably affect alcohol precipitation, but at pH 4 to 5, small pH perturbations drastically affect precipitation and index modulation amplification.

SECTION 7

DEHYDRATION AGENTS

Since the discovery of DCG as a phase holographic material, there have been few changes suggested for film development techniques. Basically, the development consists of the application of two liquids to the holographically exposed film. The first liquid is used to swell the gelatin and remove unreacted dichromate salts from the film. The second liquid removes the swelling water and collapses the gelatin film to near its original dry thickness.

The traditional water/alcohol sequence for development is still in popular use. Alternate dehydration liquids, however, have been suggested for the second liquid of the two-liquid development process.[37] These liquids include acetone, methyl ethyl ketone, ethanol, methanol, dioxane, and polyglycol ethers. Physically, these liquids are good solvents for water and nonsolvents for gelatin. Chemically, these liquids generally possess the hydroxy functional group either in its own right or through keto-enol tautomerism.

Previous literature on holographic use of DCG usually refers to the second development step as strictly a "dehydration," without much consideration for the chemical species used to accomplish it.[42-45] Generally, the dehydrating liquids suggested in the literature are alcohols (e.g., methanol, ethanol, 2-propanol), polyalcohols (e.g., ethylene glycol, glycerol), or substances that partially contain a hydroxyl group (e.g., acetone by keto-enol tautomerism). We believe that the hydroxyl group of the dehydrating liquids is chemically involved in the index modulation amplification during development since holograms dehydrated by other means, such as by (1) slow air drying, (2) fast forced hot air drying, or (3) trichloroethane vapor degreaser drying, do not show index modulation amplification. This is substantiated by

Meyerhofer,[46] who has observed an absorption peak in the near ultraviolet that he attributes to isopropyl alcohol molecules securely bound to reduced chromium sites.

We tried several new liquids that are chemically similar to alcohols for dehydrating DCG holograms. The liquids, however, differed substantially in development performance from the usual alcohols. The holographic development process up to the point of dehydration consisted of exposing DCG reflection holograms, swelling the films in deionized water, and wiping excess water from the plates.

In the same way as sulfur occupies a place just below oxygen in the periodic table, the thiols or mercaptans are sulfur analogs of alcohols. For the first class of dehydration liquids, we attempted to use these compounds as substitutes for DCG development dehydration. Since the solubility of water in ethanethiol and 1,2-ethanedithiol is low, we used large quantities of these liquids in relation to the water contained in the gelatin film. The thiol-developed holograms showed much lower diffraction efficiency than those developed in the usual propanol. Hence, we feel that the use of mercaptan dehydrating agents cannot be recommended in place of alcohol.

For another class of compounds, we kept the hydroxy functional group intact and changed the hydrocarbon part of the molecule. The first compound was 1-butanol, which has one more carbon than does propanol. The dehydrated holograms were very milky and cracked, probably due to the increased hydrophobicity of this liquid. An increase in the size of the hydrocarbon portion of the dehydrating molecule to cyclohexanol, liquefied by raising the temperature, produced very weak and clear holograms. Apparently, monofunctional alcohols larger than butanol are either incapable of penetrating the gelatin surface or their water miscibility is not high enough to dehydrate the film adequately.

We also tried DCG dehydration with halogenated alcohols that are approximately the same molecular size as the alcohols but of a higher molecular weight. We expected that the problem of getting the alcohol into the swollen gelatin could be approached by using the alcohol derivatives that have a higher dielectric constant than the parent isopropyl alcohol. Since the dehydrating agent 1-chloro-2-propanol is infinitely miscible with both water and alcohol, it appeared to be a good agent for film penetration and dehydration. However, when it was applied in holographic development, the film layer was degraded and distorted severely. Reflection holograms could not be fabricated; only transmission holograms could be obtained. Apparently, the dehydrating chlorinated alcohol has enough solvent power for the gelatin, and during dehydration enough film disruption occurs to erase the high spatial frequency reflection holograms. Under conventional development conditions, DCG displays index modulation amplification that is relatively independent of spatial frequency.[7] When 3-chloro-1-propanol was used in holographic development, the results were qualitatively the same as with 1-chloro-2-propanol. Only low spatial frequency transmission holograms could be produced.

Since acetone and other ketones can be used as dehydrating agents, we decided to try a multi-carbonyl compound that would chemically resemble acetone. The compound, 2,3-butanedione is very soluble in both water and alcohol, and its dehydrating properties appear to be well suited for DCG development. However, 2,3-butanedione, like 1-chloro-2-propanol, has a very high solvent power for gelatin. The developed films were sticky to the touch and only low-spatial-frequency holograms could be obtained.

From these results, obtained on various dehydrating agents, we conclude that 2-propanol is still the preferred dehydrating liquid. It is possible that with increased or decreased prehardening of the gelatin layers some of the processing methods for the tested compounds may be optimized to produce reflection holograms with reasonable noise levels. Our conclusion is that the lower primary alcohols, particularly 2-propanol, are the best dehydrating agents for DCG holograms.

SECTION 8

MECHANISM OF IMAGE FORMATION

The understanding of the mechanism by which DCG generates efficient holographic gratings is of critical importance to providing an approach to index modulation improvement. Two basic models for the mechanism of image formation have been proposed; for conveience, these are referred to here as the Shankoff[42,45] (crack or void) model and the Meyerhofer[46]-Case[47] (small aggregate) model. The void model postulates a series of cracks formed by the rapid alcohol dehydration of the gelatin layer, located between the highly exposed interference fringe planes. The small aggregate model is based on the formation of index modulation on a much smaller scale in producing either a multitude of small vacuoles (on the order of molecular size)[47] or a specific chemical compound formed by alcohol molecules bound to reduced chrominum sites.[46] Since there is ample evidence supporting the existence of both the crack and aggregate models, one or both models may, depending on the circumstances, apply to a particular hologram. Therefore, as we present experimental data in this section about image formation mechanisms in DCG, it is important to keep in mind the mechanism that is thought to apply in each case.

With certain DCG films and development procedures, the image can, indeed, be composed of cracks between the fringe boundaries. If the image is recorded as cracks, and if the index modulation is represented as a Fourier expansion of a periodic waveform, then the discontinuities between fringe foundaries (i.e., cracks) would show up as large higher-order Fourier coefficients beyond the fundamental frequency. Recently, from measurements made on DCG hologram efficiency and angular selectivity, Case[47] has calculated that large cracks between fringe boundaries appear to be unlikely because of the absence of higher-order Fourier coefficients in the index modulation.

From this evidence and our own observations, we must conclude that both image types are possible, depending on the process used for DCG hologram fabrication. We have observed that, with reflection holograms, both types of images may be present simultaneously and be easily identified.[27,48] The first type of image appears as a highly efficient, although noisy, hologram that reconstructs at wavelengths typically longer than that at which it was recorded.[49] This image type frequently contains discontinuities that follow outlines corresponding to lines where fringes should meet the surface of the film. We believe that this image is caused by cracks in the interior of the gelatin film and that the apparently high index modulation results from the refractive index differential between air ($n = 1.00$) and gelatin ($n \approx 1.54$).

The second type of phase, or aggregate, image formation can be observed as a lower diffraction efficiency image, appearing with very low scattering noise. We postulate that the index modulation in this case is formed by high refractive index centers or chemical aggregates formed within the bulk of the film, corresponding to light-exposed areas.

A reflection hologram lens having both types of image mechanisms is shown in Figure 35. Most of the hologram appears as a uniformly diffracting area of relatively lower diffraction efficiency. The cracked image shows up as narrow, long, curved areas of higher diffraction efficiency. These areas correspond to the places where fringe line cracks meet the surface and utilize the index differential between air and gelatin. Under the microscope, the cracked images can be distinguished from the aggregate image by the "onion-skin" appearance of the cracked material.[45]

The aggregate image in reflection holograms can be distinguished from the cracked image by its response to elevated temperatures. When low-efficiency DCG holograms are destructively tested by heat treatment, the low-noise aggregate image shows a typical response such as shown in Figure 36. The hologram is stable up to about 110°C, after which it

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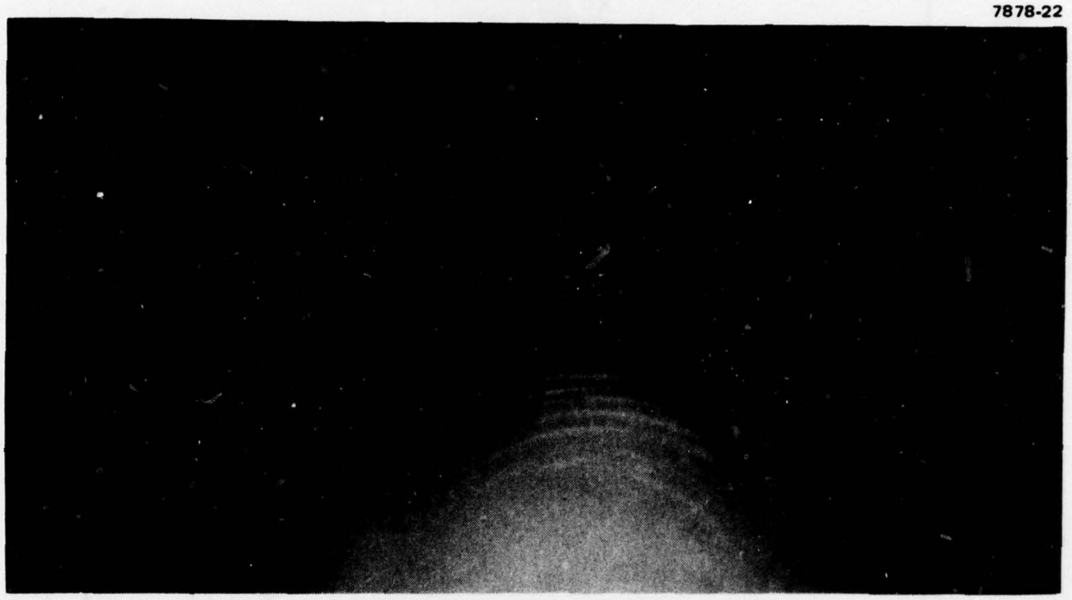

Figure 35. Photograph of a reflection from a DCG reflection lens hologram, formed by a plane wave and spherical wavefront, showing the presence of both cracked and uncracked (aggregate) images.

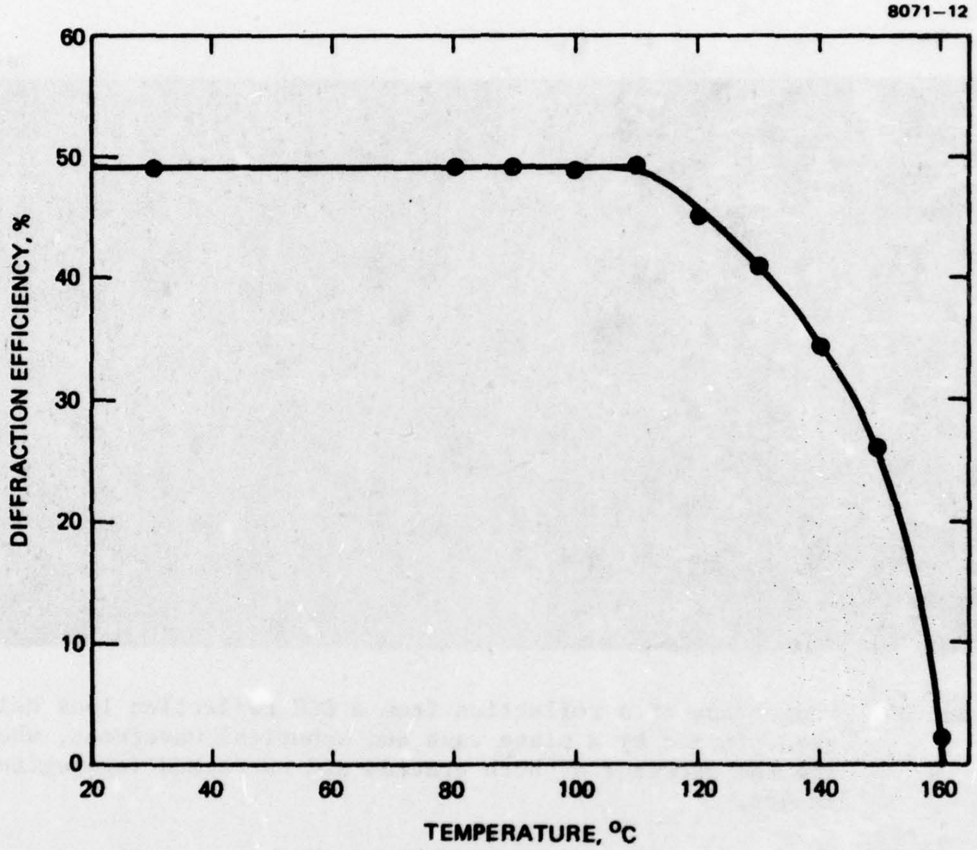

Figure 36. Diffraction efficiency destruction in low-efficiency reflection holograms with high temperature.

degrades rapidly. Diffraction efficiency drops steadily and peak reflective wavelength drifts to the green-blue spectral region. We feel that it is highly unlikely that large cracks in the gelatin would behave in this manner. More likely, at the elevated temperatures, certain events on a molecular level take place, such as either small voids closing by molecular rearrangement or bound alcohol molecules being released from reduced chromium sites.

In a similar high-temperature test, we stressed highly cracked reflection holograms. These holograms behaved quite differently from their low-efficiency counterparts. At about 182°C, efficient holograms still persisted although the peak reflective wavelength had changed to blue-violet, indicating film thickness collapse and retention of index modulation.

At 204°C, the reflection holograms disappeared and the color of the gelatin films turned to light brown. We believe that degradation and oxidation within the gelatin matrix caused sufficient changes to fill in the high spatial frequency reflection hologram cracks. Low diffraction efficiency transmission holograms (ghost images) still persisted at 204°C, showing that the destruction of holographic gratings by high temperature is probably dependent on the spatial frequencies of the gratings involved. In general, the higher the spatial frequency of a grating, the easier it is to degrade it by heat.

The small aggregate model, containing a specific DCG chemical species,[46] appeared to apply to holographically exposed DCG films before chemical development when relative humidity changes are considered. Relative humidity influences gelatin film thickness, since the protein absorbs moisture at high humidities.[50] Therefore, we would expect that, if the air moisture were uniformly absorbed in a hologram, diffraction efficiency would vary as the film thickness times index modulation. However, when, for example, a 12-μm-thick DCG film is holographically exposed in a transmission geometry at 40% relative humidity (RH), it develops about 3% diffraction efficiency, as shown in Figure 37. If the hologram is exposed at 77% RH, efficiency will increase to 9% without further light exposure. Moreover, this efficiency increase can be reversed by going back to 40% RH. Hence, we observe about a threefold increase in diffraction efficiency in going to 77% RH, whereas the film thickness changes by only about 10%.[17] These changes in diffraction efficiency can be explained in terms of changes in index modulation in response to changes in RH.

When a reflection hologram is exposed with its interference fringes parallel to the plate substrate, we would expect the peak reflective wavelength after processing to return to near the exposure wavelength.[51] If the image is recorded within the bulk of the film strictly as a different chemical species, then we would expect to see the same peak reflective wavelength to be shown for any amount of index modulation. If, however, the image is recorded as voids or vacancies within the gelatin film, then the peak reflective wavelength will increase with increased index modulation. This is because increased index modulation can come from increased voids in the gelatin film. These voids occupy space and hence force the film to swell to larger wavelengths. Figure 38 does, indeed, show that the peak reflective wavelength increases almost linearly with index modulation. This further demonstrates that actual voids occur within the gelatin film to form the holographic image. Figure 39 shows that the diffraction efficiency of a reflection hologram increases as a function of time after development and that the peak reflective wavelength decreases simultaneously. If the index modulation increase in the hologram can be attributed strictly to the evaporation of alcohol from film vacancies or voids, then the reflective wavelength should remain constant. However, since we do observe reflective wavelength changes along with changes in diffraction efficiency, it appears that the gelatin itself must be undergoing geometrical and index changes.[52] We believe that the gelatin molecular strands, during the period after development, undergo packing factor changes and become more closely packed. This is manifest in the decrease of the reflective wavelength of the holographic films.

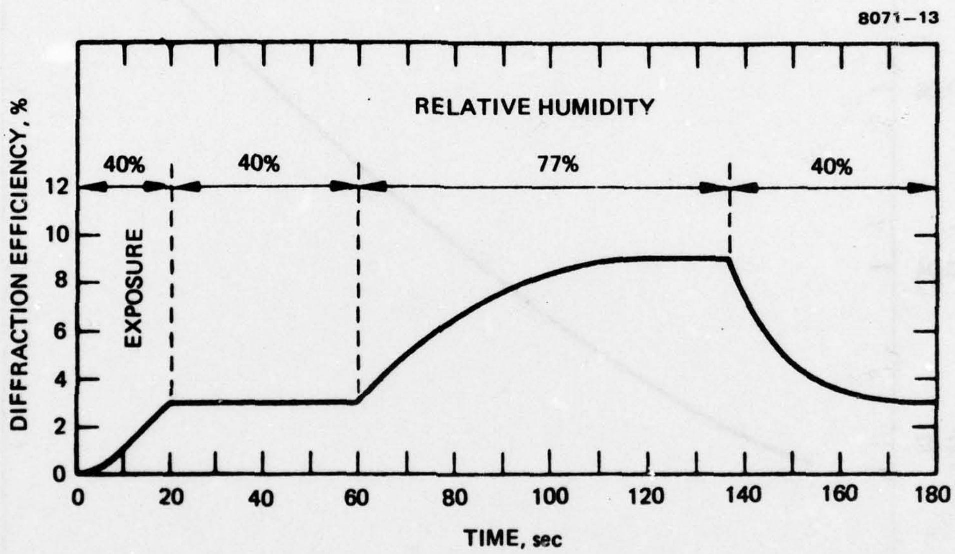

Figure 37. Light diffraction efficiency of a 12-μm-thick DCG film during holographic exposure in different relative humidities.

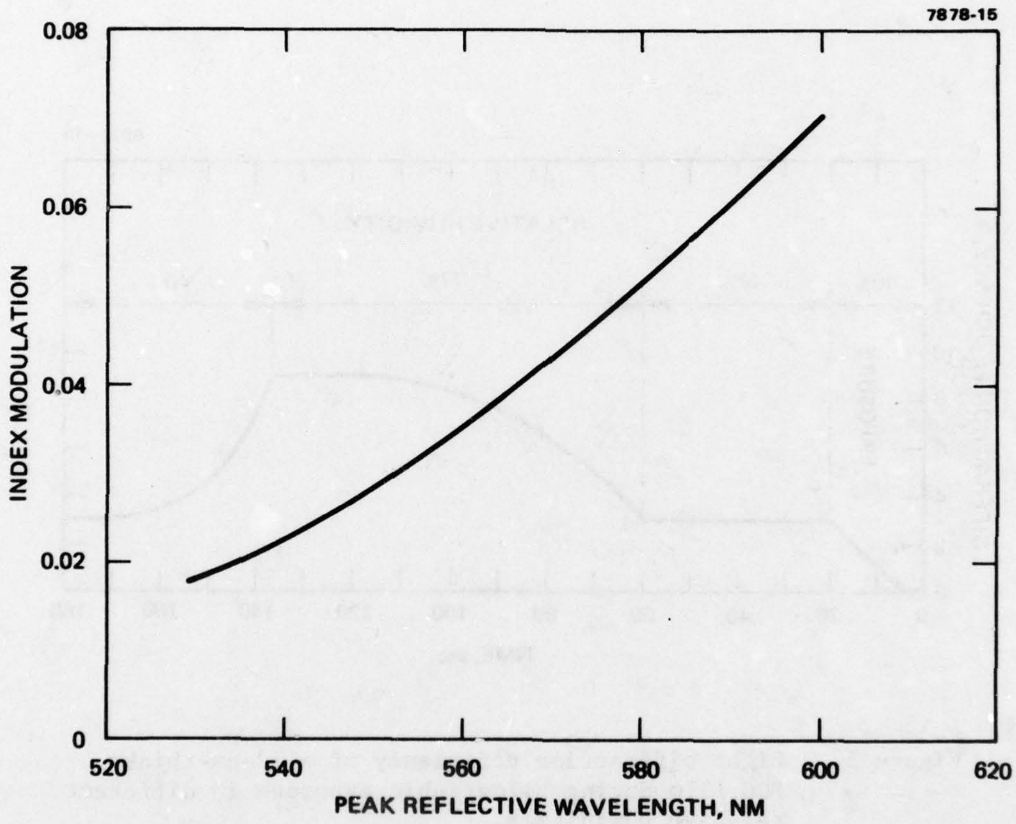

Figure 38. Holographic index modulation increases as a function of peak reflective wavelength.

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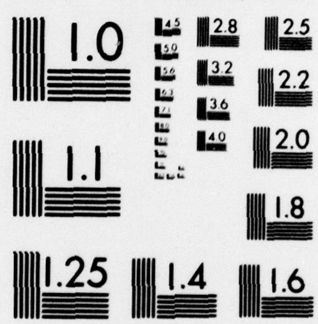

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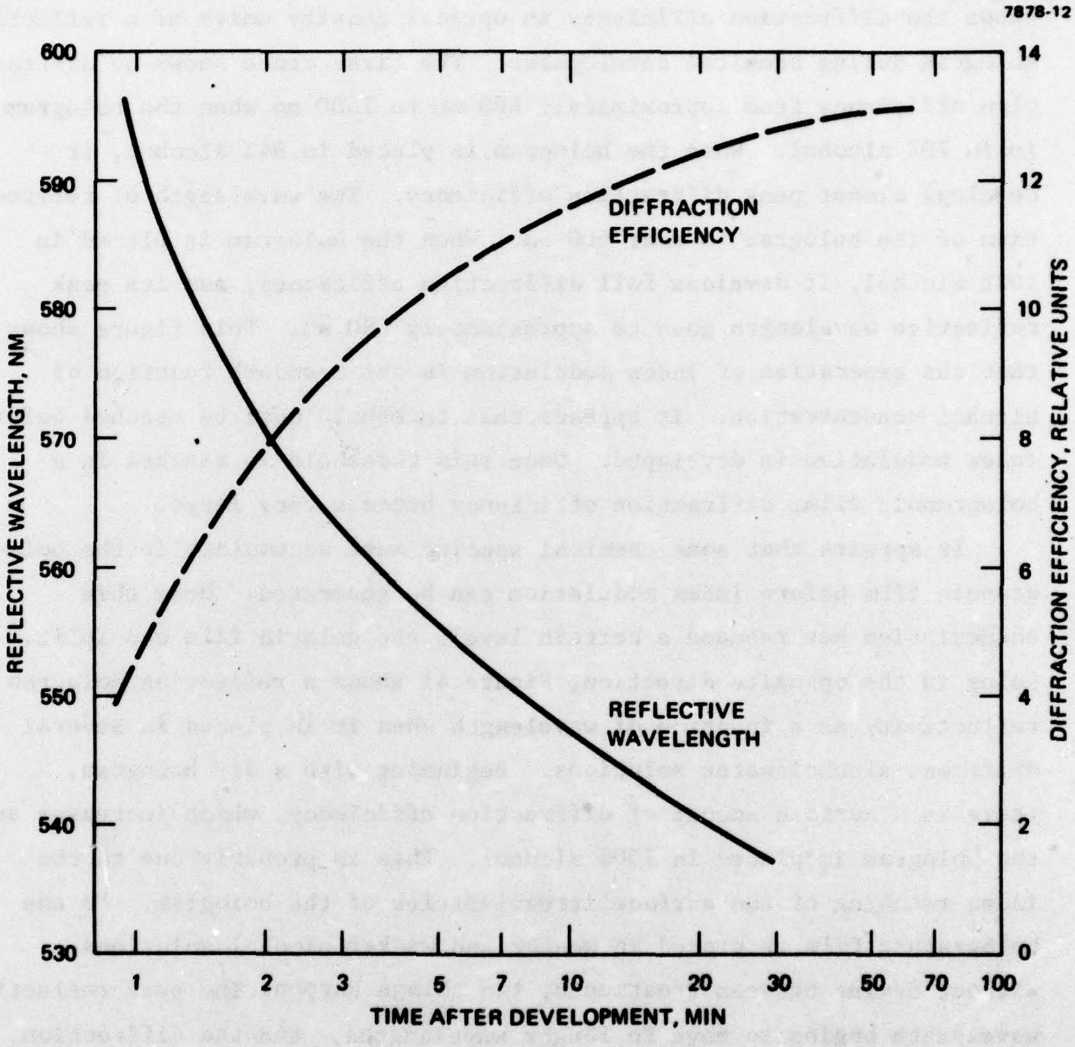

Figure 39. Light diffraction efficiency and peak reflective wavelength changes in a DCG hologram as a function of time after development.

The appearance and disappearance of diffraction efficiency in DCG holograms shows a step function in alcohol development baths. Figure 40 shows the diffraction efficiency in optical density units of a reflection hologram during chemical development. The first trace shows no diffraction efficiency from approximately 400 nm to 2400 nm when the hologram is in 70% alcohol. When the hologram is placed in 94% alcohol, it develops almost peak diffraction efficiency. The wavelength of reflection of the hologram is near 600 nm. When the hologram is placed in 100% alcohol, it develops full diffraction efficiency, and its peak reflective wavelength goes to approximately 580 nm. This figure shows that the generation of index modulation is not a smooth function of alcohol concentration. It appears that threshold must be reached before index modulation is developed. Once this threshold is reached in a holographic film, diffraction efficiency becomes very large.

It appears that some chemical species must accumulate in the holographic film before index modulation can be generated. Once this accumulation has reached a certain level, the gelatin film can split. Going in the opposite direction, Figure 41 shows a reflection hologram reflectivity as a function of wavelength when it is placed in several different alcohol/water solutions. Beginning with a dry hologram, there is a certain amount of diffraction efficiency, which increases as the hologram is placed in 100% alcohol. This is probably due to the index matching of the surface irregularities of the hologram. As the holographic film is placed in weaker and weaker alcohol solutions, without drying between treatments, two things happen. The peak reflective wavelength begins to move to longer wavelengths, and the diffraction efficiency decreases markedly in going from 98% alcohol to 90% alcohol. The peak reflective wavelength appears to go to zero at about 600 nm. Apparently, the step function that we observed in Figure 40 in going from weak to strong alcohol solutions is somewhat reproducible in going in the other concentration direction. This again points to a physical mechanism of film healing during the application of water/alcohol solutions.

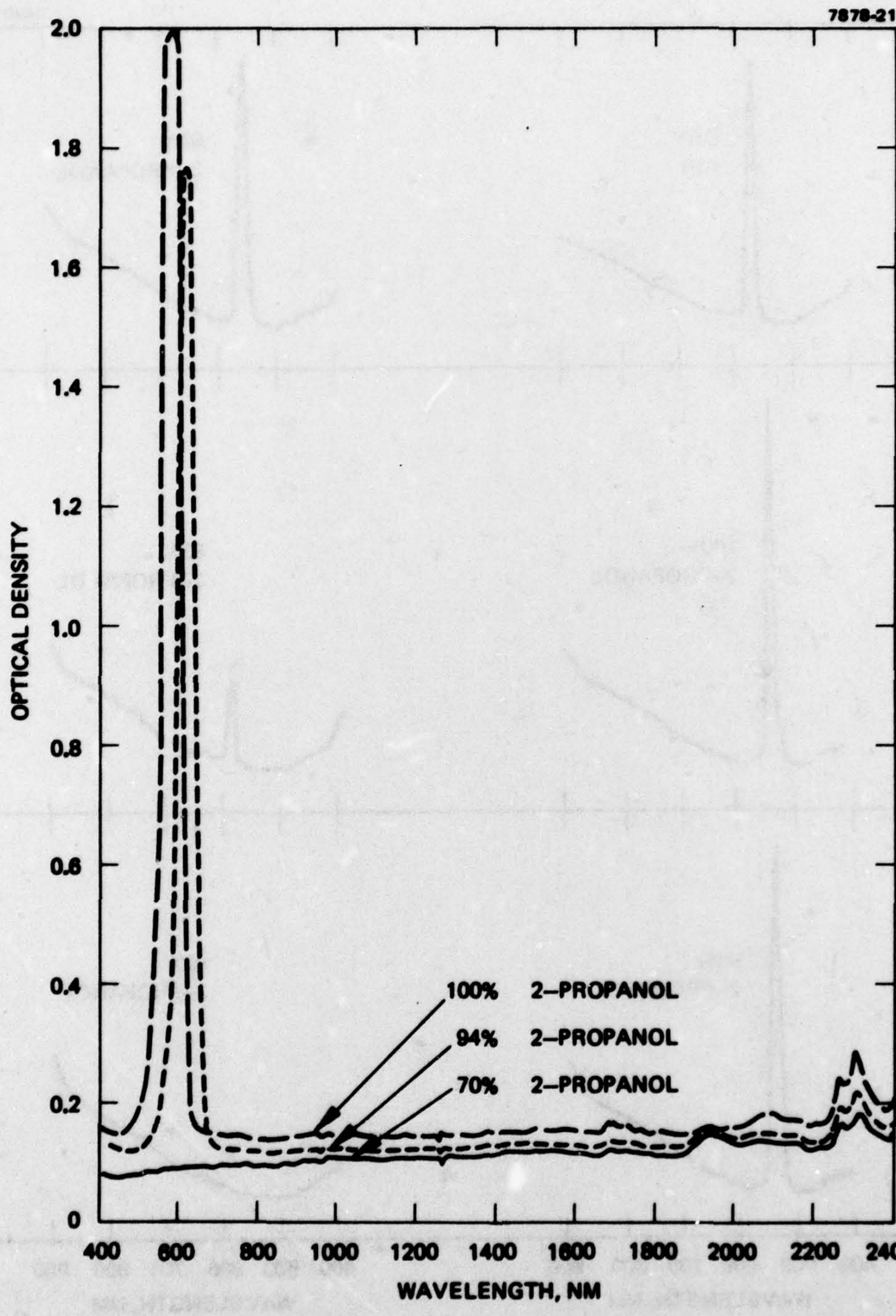

Figure 40. Generation of light diffraction efficiency in optical density units in various alcohol baths during hologram development.

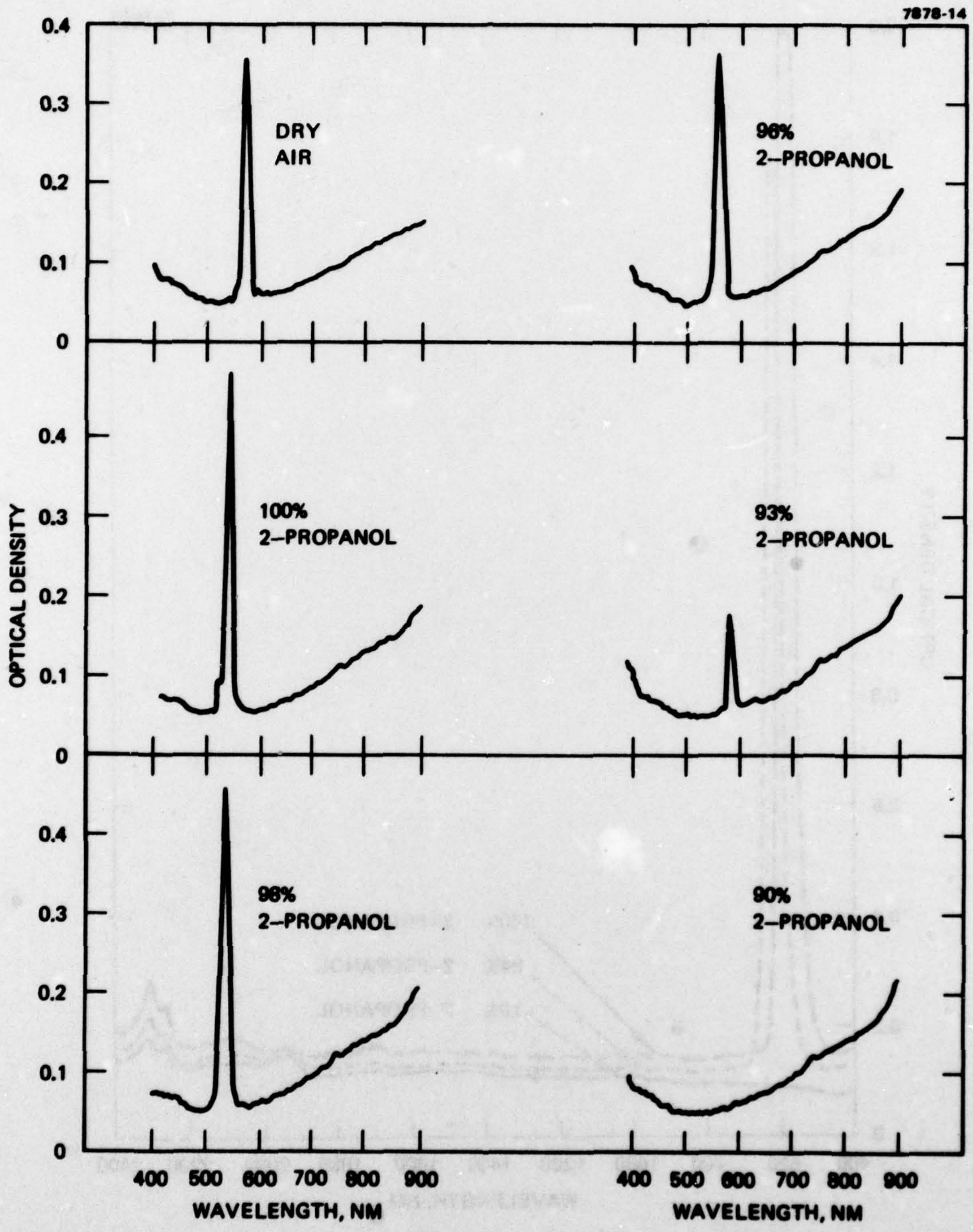

Figure 41. Distruction of light diffraction efficiency in optical density units by the application of aqueous-alcohol solutions.

In another experiment, we demonstrated the existence of voids in a holographic film. A fully developed reflection holographic plate was subjected to mechanical pressure perpendicular to the fringe planes and the substrate glass. Figure 42 shows the diffraction efficiency of a reflection hologram as a function of wavelength as it is mechanically pressurized. Without pressure, the hologram exhibits good diffraction efficiency (in optical density units) peaking at approximately 540 nm. When 250 psi are applied to the hologram, both the diffraction efficiency and the peak reflective wavelength decrease substantially. With 2000 psi, the hologram is almost totally obliterated and the peak reflective wavelength is reduced to 425 nm. We postulate that the index modulation in the film is either contained in pressure-sensitive molecular species or in actual voids within the DCG hologram. We are most likely encountering in these holograms actual voids that lie parallel to the substrate.

In a final experiment, we tested the possibility of alcohol remaining in the holographic film after development. We tried to correlate the amount of alcohol in the film with the diffraction efficiency or index modulation. We first tested four transmission holograms ranging in diffraction efficiency between 5% and 80%. The holograms were soaked in 1 ml of water to remove alcohol from a 6 cm^2 area of the 10-m-thick film. The resulting water solutions were tested by gas chromotography for the presence of alcohol. No alcohol was detected in these films. The detection limit for the gas chromatography is 1 ppm. In a second experiment, reflection holograms were used. These holograms had been developed similarly to the transmission holograms and had been stored for over a year without any cover plate protection. We assumed that this time would be long enough to allow any residual alcohol to evaporate from the films that was not chemically constrained to remain there. When a non-image film area was leached with water, 3 ppm of isopropyl alcohol was detected in the extraction water. In a second film area, where a very efficient (i.e., cracked) image was present, 6 ppm of

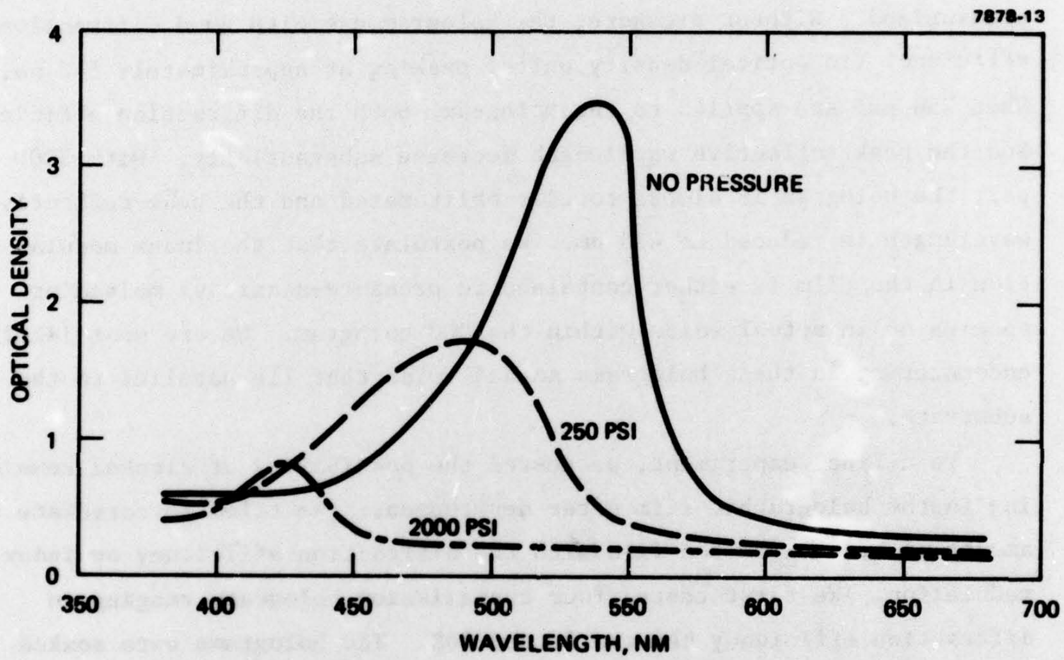

Figure 42. Mechanical pressure can collapse a Lippman holographic DCG grating.

isopropyl alcohol was detected. When we leached a hologram with about 70% diffraction efficiency with water, 199 ppm of isopropyl alcohol was detected. Calculation revealed that the amount of alcohol leached from the film was approximately 1.7 wt% of the gelatin. If the average molecular weight of a pigskin gelatin amino acid residue is calculated to be 90.4, then there are 38.5 residues of gelatin per alcohol molecule in the film. Since one of approximately 8.5 gelatin amonio acid residues are acidic groups such as glutamic and aspartic acids, 1 out of every 4.5 acid functional groups may be occupied or esterified by alcohol if alcohol is found at those sites. More probably the alcohol is held by hydrogen bonds since water application will remove it from the film. We believe that the presence of alcohol functional groups, although initially necessary in development to amplify index modulation, is not vital after small or large cracks have been formed. Residual alcohol escapes quickly from either large cracks in reflection holograms or from even small cracks in transmission holograms (where diffusion distances are small due to fringe geometry). Alcohol is only retained in small aggregate images in reflection holograms where its escape is prevented by the fringe geometry.

From all of these data, we postulate an image formation mechanism in DCG that is consistent with the phenomena observed. This mechanism is believed to be based first on chemical species residing within the gelatin film. Second, the chemical development transforms this chemical image into a physical image consisting of small vacuoles and cracks. If the holographic development becomes more severe, either through added solutes, pH changes, or elevated temperature, large cracks are formed.

When a dry gelatin film containing dichromate is exposed to actinic radiation, the dichromate ion becomes photo-excited and susceptible to reduction by the gelatin film. The products of the reduction cross-link individual peptide chains.[53] Shown in a simplified way in Figure 1, the reduced dichromate compound cross-links form the chemical basis for image formation in DCG. This chemical image is manifest in its water-absorption characteristics, as shown in Figure 37 and discussed by Curran.[45] This chemical image, however, contains little index modulation. With swelling in water, the index modulation can be as high as approximately 0.0005. The real magic of DCG holograms takes place in the development. In the DCG development process, after the film has been washed and expanded in water, the alcohol bath affects the film in two ways: (1) it collapses the film by osmotic dehydration, and (2) it simultaneously diffuses alcohol molecules into the layer to displace water from the interior of the film. The water displacement by the alcohol is different for exposed and unexposed regions of the film. When the alcohol concentration becomes high enough in the interior of the film, low-refractive-index centers develop. These may be chemical in nature, but more probably they are actual small voids within the interior of the film. Figure 40 shows that the alcohol concentration must be greater than 70% to cause the appearance of this type of image. Once the image is formed, larger concentrations of alcohol do not increase diffraction efficiency by very much, nor does the reconstruction wavelength in reflection holograms change appreciably. What we have, then, is a situation where small voids are formed in the interior of the film, making the recording appear to be essentially grainless because the voids are on the order of molecular dimensions. The small voids can be healed, as shown in Figure 41, by placing the hologram in weaker alcohol solutions and allowing water to diffuse into the holographic film. These voids can also be collapsed by direct pressure, as shown in Figure 42, where approximately 2,000 psi decreases the diffraction efficiency to almost zero. The existence of these small voids was substantiated by Case[47] as a lowering of overall film refractive index. Higher-order Fourier coefficients are not present in the index modulation profile of lightly exposed DCG films, showing that the index modulation distribution more closely resembles a sine than a square-wave function.

There exists considerable evidence for small voids in low efficiency holograms, where only a small fraction of the index differential between air and gelatin is utilized. Meyerhofer[46] points to the inability of the large crack theory to account for several phenomena that he has observed, such as the recording of multiple holograms in a single emulsion layer. Most of the index modulation in small voids is probably not of a chemical nature. Case[47] points to the decrease in index modulation in DCG with increasing exposure energy. It is doubtful that a chemical species attached to the gelatin or embedded in the gelatin would acquire a high index radically different from that of the parent film layer. The small voids in a holographic image can at times become so large that they fuse together to form single large cracks at fringe boundaries. Curran[38] amply demonstrates the existence of large cracks in DCG holograms with particularly harsh development methods. We feel that the transition between small voids and gross cracks in DCG holograms is smooth in transmission holograms and very abrupt in reflection holograms. When the diffraction efficiency of a low spatial frequency transmission hologram is plotted as a function of exposure, the curve is sinusoidal shaped,[54] showing that there are no abrupt discontinuities between an increase in index modulation and exposure. In reflection holograms, however, the fringe boundaries do not intersect the substrate as frequently as in transmission holograms. Therefore, the cracks are not constrained by the substrate material. Figure 35 shows that the cracking in reflection holograms can take place in discrete film areas. Further, Figure 14 shows that in the small aggregate image that is formed between development baths of pH 2 to approximately 12, the diffraction efficiency remains low. Below pH 2, the small voids fuse into large cracks, and much larger efficiencies are gained that utilize more of the index differential between gelatin and air. This theory accounts for all of the phenomena observed with DCG holograms. The inclusion of a chemical image species, a small void species, and large cracks makes the theory universally applicable.

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